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(21) International Application Number: PCT/GB97/01170 (22) International Filing Date: 29 April 1997 (29.04.97) (30) Priority Data: 08/639,960 29 April 1996 (29.04.96) US (71) Applicant (for GB only): MATTHEWS, Derek, Peter [GB/GB]; 67 Lavington Road, London W13 9LR (GB). (71)(72) Applicant and Inventor: SIPPEL, Roy, Joseph [US/US]; 153 Pierson Road, Woodstown, NJ 08098 (US). (72) Inventors: FENG, Ke; 351 Wiley Circle, Lilburn, GA 30247 (US). PASEK, Eugene; 115 Maple Place, Fayetteville, GA 30215 (US). (74) Agents: MATTHEWS, Derek, Peter et al.; Frank B. Dehn & Co., 179 Queen Victoria Street, London EC4V 4EL (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SALT OF BOEHMITE ALUMINA (57) Abstract A cationic fibrous acetate salt of boehmite alumina useful in dyeing fabrics. <div style="text-align: right; font-family: cursive; font-size: 2em; margin-top: 20px;">floculant Page 4 additional floculants</div>		

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SALT OF BOEHMITE ALUMINA

5 The present invention relates to a cationic fibrous acetate salt of boehmite alumina, a method for its preparation, its use in dyeing fabrics e.g. cotton and for removing waste from waste streams e.g. waste streams containing dyes.

10 Generally, dyeing is accomplished by placing a solution containing a dye in contact with fibers or fabric composed of many fibers whereby dye is entrapped within or attached to the lattices of the entwined fibers. The fibers or fabric are then washed to remove
15 unfixed dye, i.e., dye which is not fully attached or trapped. In the past, untrapped or unattached dye was discharged as waste effluent along with the spent dye bath, which has a higher concentration than the washing effluent. Not only was a considerable quantity of
20 valuable dye lost but the effluent needed to be treated before being discharged into streams. The word dye as used herein includes dyestuff and formulations or combinations of dyes and carriers, fillers, and the like.

25 The present invention relates to a salt of boehmite alumina suitable for use in dyeing and in purifying a waste stream or effluent. The present invention also relates to purification of municipal and dye waste streams by flocculation and/or precipitation. In the
30 dyeing of fabrics, the ability of a material useful in the dyeing process to remove a substantial amount of dye from the dye waste stream serves to improve efficiency and reduce treatment costs.

35 It has been found that placing a novel cationic fibrous acetate salt of boehmite alumina (in a form such as cakes, chips, particles, plates or shaped bodies) in contact with a dye waste stream leads to flocculation or

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precipitation of the dyes without contamination of the stream with other ionic species. Thus the salt of boehmite alumina is not only useful in the dyeing process but is also capable of precipitating, associating with and/or flocculating the dyes (e.g. anionic dyes) whether the dye is present as a contaminant in a municipal waste stream or as residual dye (which was untrapped by or unattached to fibers) in a dye bath waste stream. Optionally the removed dye may be recycled to the dyeing process.

Thus viewed from one aspect the present invention provides a cationic fibrous acetate salt of boehmite alumina obtainable by stirring a slurry of water and basic aluminium acetate to ensure substantially complete mixing thereof, reacting the slurry to produce a fibrous cationic acetate salt of boehmite alumina having a zeta potential of greater than about 25 and a weight ratio of aluminium to acetate of less than about 4.

One advantageous feature is that the surface area to volume ratio of the salt according to the invention can be about 50% or greater.

Advantageously, the fibrous acetate has at least about 40% more active/reactive sites than commercially available colloidal alumina.

Viewed from a further aspect, the invention provides a method for preparing a cationic fibrous acetate salt of boehmite alumina according to the invention comprising: stirring a slurry of water and basic aluminum acetate to ensure substantially complete mixing thereof, reacting the slurry to produce a fibrous cationic acetate salt of boehmite alumina having a zeta potential of greater than about 25 and a weight ratio of aluminum to acetate of less than about 4.

Advantageously the slurry contains (on the basis of Al_2O_3) from about 0.5 weight % to about 30 weight % Al_2O_3 , preferably from about 0.5 weight % to about 15 weight % Al_2O_3 . Advantageously, the slurry is stirred for from

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less than about 1 minute to about 60 minutes prior to initiating the reaction, preferably from about 5 minutes to about 30 minutes. Advantageously, the slurry is reacted at a temperature of from about 100°C to about 180°C, preferably from about 140°C to about 160°C and is reacted for a time of from less than about 1 second to about 240 minutes. Depending on the type of final product desired, the slurry can be reacted for a time of from about 10 minutes to about 120 minutes. Advantageously, the slurry is reacted at a temperature of about 140°C for about 120 minutes for one type of final product. Another type of product is produced where the slurry is reacted at a temperature of about 153°C for less than about 5 seconds, wherein the slurry temperature increase is halted and cooling is started when the slurry temperature reaches 153°C. Advantageously the slurry is stirred during the reaction at a rate of from about 50 to about 800 rpm. After completion of the reaction, the reacted slurry is advantageously cooled to a temperature of from about 20°C to about 100°C.

The present invention further provides a process for dyeing fibers with a dye selected from the group consisting of direct, reactive, sulfur and acid dyes comprising: passing undyed fibers through a bath containing dye which is associated with or attached to a cationic fibrous acetate salt of boehmite alumina according to the invention whereby the fibers remove the dye from the fibrous acetate salt of boehmite alumina upon contact therewith.

In another aspect, the present invention provides a process for treating a dye waste stream comprising the steps of introducing into the stream at least one flocculating or precipitating agent comprising a cationic fibrous acetate salt of boehmite alumina according to the invention; forming a precipitate or flocculant of the dye and agent; and separating said

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precipitate or flocculant from the stream. The flocculating or precipitating agent itself forms a further aspect of the invention and may further comprise components selected from the group consisting of
5 inorganic salts, coagulants, organic flocculants, polymeric flocculants and mixtures thereof.

Although the dyeing and dye removal process will be explained relative to direct dyes, it should be understood that the processes are equally applicable to
10 other dyes, e.g. direct, acid, sulfur or reactive dyes, any dye that has a negative charge or partial negative charge.

In the treatment process the agent advantageously has an ionic charge opposite to that of the dye
15 contained in the dye waste stream whereby the dye is attached to the agent by ionic substitution. Preferably the agent has a positive ionic charge and the dye has a negative ionic charge. Preferably the process includes the step of adjusting the pH of the waste stream and
20 fibrous acetate suspension to between about 2 and about 8. The precipitate or flocculant is conveniently removed by flotation separation and filtered and may include the step of separating the dye from the precipitate or flocculant and the step of regenerating
25 the dye from the precipitate or flocculant. Such regeneration may be achieved by contacting the precipitant or flocculant with a negatively charged group such as for example OH^- or CO_3^{2-} . Optionally the separated or regenerated dye is reused in the dyeing
30 process.

A further aspect of the present invention is a process for removing contaminants from a municipal waste treatment stream which comprises: adding a cationic fibrous acetate salt of boehmite alumina according to
35 the invention to the waste stream; forming a precipitate or flocculant of the contaminants and the salt; and separating the precipitate or flocculant from the waste

stream.

Prior to the present invention the dye waste stream was typically treated and discharged as effluent. Using the present process one can remove the dye, optionally regenerate the dye, and reuse or discharge the substantially dye-free stream.

Advantageously, the ionic charge of the fibrous acetate salt of boehmite alumina is opposite to that of the dye. Preferably the fibrous acetate has a positive charge and the dye has a negative charge. Since the dye is negatively charged, it is attracted to and attaches to the positively charged fibrous acetate. The differences in the charges result in a high degree of reactivity or attachment between the dye and the fibrous acetate. Although the adsorption of the dye onto the surface of the fibrous acetate accounts for a portion of the unexpectedly superior results of the fibers of the present invention, it is believed that the reactivity resulting from the difference in charge between the fibrous acetate and the dye is in a large part responsible for the unexpected results evident in the removal of a substantial portion of the dye from the waste stream.

Preferably, the pH of the waste stream is adjusted to between about 2 and about 8 by the addition of mineral acids or organic acids to aid in the precipitation or flocculation of alumina acetate monohydrate salt fibers and dye. The dye (excluding reactive dyes) may be regenerated or separated and recycled to the dyeing process. Particularly preferred results are obtained when the waste stream has a pH of between about 3 and about 5. A sufficient quantity of fibrous acetate can be added to the dye waste stream in any convenient manner.

One method of separating the precipitate or flocculant is by the use of a flotation separator. Flotation of the particles may be achieved by

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supersaturation with air under pressure. The pressure is then released and the air in the suspension lifts the particles to the surface. The floating particles are then removed by a mechanical skimmer and the waste
5 decolorized effluent discharged. The particles may then be recycled and used in the dyeing process by any convenient means. The concentration of the particles can also be increased by filtration through a filter. A
10 large percentage of the alumina monohydrate fibers used in the precipitation or flocculation process can be easily recovered. While flotation separation is a preferred method of separation, the removed dye can be separated by other methods known to the skilled man such as high pressure filtration. However, high pressure
15 filtration requires more energy than the flotation separation.

An important aspect of the present invention is the possibility that the dye in certain instances can be regenerated, returned to the dyeing process and reused.
20 As discussed above, it is believed that solubility based on the differences in charge between the fibrous acetate and the dye is largely responsible for the unexpected results of the present invention. The dye may be regenerated by substituting a negatively charged group
25 for the negatively charged dye, thereby releasing the dye from the fibrous acetate. Advantageously such negatively charged group is an OH^- , CO_3^{2-} , or the like alkaline group. Preferably the precipitate or flocculant is filtered and a negatively charged group is
30 used to contact the filter cake containing the alumina acetate monohydrate salt fibers and dye, thereby substituting the negatively charged group for the dye and releasing the dye to be reused.

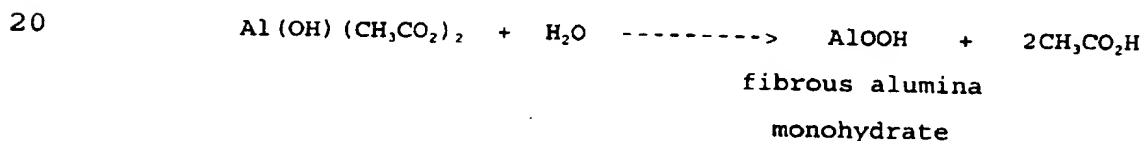
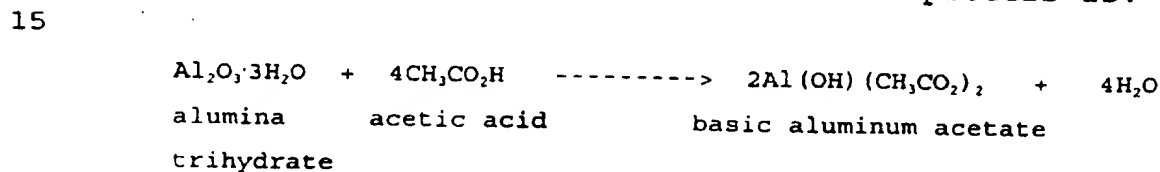
The process according to the invention for removing
35 dye from waste streams containing dyes may be batch or may be operated on a continuous basis.

In commercial processes the dyeing of fabric can be

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an environmental hazard. Commercial processes require heating of the dye bath up to 90°C and adding, up to 10% sodium salt, as either chloride, or sulfate for proper coloration. Application of the fibrous alumina acetate in accordance with the invention before dyeing the fabric (pre-treatment) can reduce or eliminate the need for heating the dye solution and the need for salt addition.

The salt according to the invention may be prepared from basic aluminum acetate which itself may be prepared from alumina trihydrate and acetic acid. With elevated temperature and pressure, basic aluminum acetate may be hydrolyzed to produce alumina monohydrate which polymerizes to form fibers. The overall process is:



The equation shows the formation of boehmite; however, the product of this invention is actually a boehmite acetate salt. Basic aluminum acetate can also be formulated as $\text{Al}_2\text{O}(\text{CH}_3\text{CO}_2)_4 \cdot \text{H}_2\text{O}$. The sol product is composed of alumina monohydrate fibers, acetic acid and water.

The reaction conditions, temperature, solids concentration, pH and stirring rate determine the dimensional characteristics of the fibers. Fibers with a range of new and unexpected dimensional characteristics have been found to be generated e.g. short and very wide or flexible and hair-like. Solid concentrations and temperature are parameters that directly impact the size and dimensions of fibers and

bundles. Bundles are large aggregations of individual fibers and are generated at specific reaction conditions.

5 **EXAMPLES**

 Whilst the highly cationic boehmite alumina acetate fibrous solution of the present invention is preferably generated in a pressure vessel (e.g. Parr reactor Model 4522M), any type of equipment that permits rapid heating and cooling of a slurry may be used. The process advantageously may be summarized in four stages:

 (1) Preparation of BAA slurry:

 1357 g of deionized water was added to 143 g of an in-house prepared basic aluminum acetate (BAA) and the slurry stirred for 10 minutes. The stirred slurry was then placed in the Parr reactor quickly to prevent any settling, the agitation set to 200-400 RPM and the heating turned to high.

 (2) Rapid heating to a mild temperature:

 The heating rate was varied from 4°C/minute initially to 5°C/minute approaching the desired temperature.

 (3) Minimal reaction time at the desired temperature:

 Once the desired temperature was reached, heating was stopped and ice water was immediately pumped into the cooling coil inside the reactor so that the solution was at the reaction temperature for less than one minute.

 (4) Cool down and discharge:

 While cold water was pumped through the cooling coil, stirring was continued. When the contents reached 50°C, pumping was stopped and the solution discharged. The cool down process took about 10 minutes.

Mild reaction temperature (140-160°C) with minimal reaction time are desired to complete the hydrolysis of BAA and restrict the growth of the boehmite alumina acetate fibers. Small fibers afford higher specific surface area as well as the desired charge density.

The alumina monohydrate sol product was dried at 350°C. The high degree of cationic character of the boehmite alumina acetate salt is responsible for its reaction/adsorption with textile dye stuffs and waste water remediation.

Characterization of the alumina acetate salt fibers was carried out by a variety of known analytical techniques e.g. scanning electron microscopy (SEM), transmission electron microscopy (TEM); thermogravimetric methods and acid titration of acetic acid content in the sols; particle size analyses; and zeta potential. In addition, textile dye adsorption maxima, elemental analysis, thermogravimetric analyses (TGA), X-ray diffraction and infrared spectroscopy have provided further insight into the nature of the alumina sols.

3.0 weight percent as Al_2O_3 sol was generated in the 2-liter Parr reactor at 140°C for 2 hours (sol A). These reaction conditions produced sols comprised of short thin fibers. A second 3.0 weight percent as Al_2O_3 sol was generated in the same reactor at 153°C with zero holding time at this temperature, e.g. the mixture was heated only to temperature (sol B). This latter material contained only very small fibers (<145nm in length (TEM)). Samples of sols A and B were air dried at ambient temperature and elemental analysis was performed for aluminum, carbon and hydrogen. TGA was run on each air dried sample using a DuPont 9900 thermogravimetric cell. In a first run, the sample was dried at 80°C for 15 minutes prior to ramping the temperature (20° per minute) to 650°C and in a second run ramping to 650°C without any drying period. Additional

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samples of the air dried sol were heated at 80°C for 17 hours and another at 350°C for 2 hours. Similarly, two air dried samples were examined by TGA experiments, one where the temperature was ramped at 20°C per minute and the other at 2°C per minute. X-ray diffraction was run on these dried sols. Infrared spectra of air dried sol were obtained.

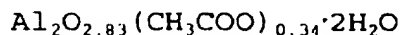
Elemental Analyses

1. Sol A

The elemental analysis of the air dried sample of sol A was C 4.92%, H 3.08% and Al 32.32%. The difference between this sum (40.32%) is considered to be oxygen: 59.68. Assuming carbon is only associated with acetate ion, the acetate content is calculated to be 12.10% apportioned as C 4.92%, H 0.62%, O 6.56%. The remaining H, O, Al content is shown below, along with the moles, normalized moles and charge balance for acetate and these elements:

ELEMENT/ION	WEIGHT PERCENT	MOLES	NORMALIZED MOLES	CHARGE BALANCE
Acetate	12.10	0.205	0.171	-0.171
Aluminum	32.32	1.20	1.00	+3.00
Hydrogen	2.46	2.44	2.03	+2.03
Oxygen	53.12	3.32	2.55	-5.10

Although the charge is not in perfect agreement (+5.03 versus -5.27), this is assumed to be due to slight errors in the elemental analyses. If it is assumed that two aluminum atoms exist in this material, e.g. that it is an alumina, the empirical formula (molecular weight 155.03 gram/mole) for the material may be written:



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2. Sol B

The elemental analysis for an air dried sample was C 8.79%, H 3.70% and Al 30.60% and for the elements (with total acetate 21.6%) was C 8.79%, H 1.10%, O 11.72%.

Thus, this sol contains considerably more acetate than sol A. The remaining percentages for the elements, along with this calculated acetate, are given below:

ELEMENT/ION	WEIGHT PERCENT	MOLES	NORMALIZED MOLES	CHARGE BALANCE
Acetate	21.61	0.366	0.324	-0.324
Aluminum	30.60	1.13	1.00	+3.00
Hydrogen	2.60	2.58	2.28	+2.28
Oxygen	45.19	2.82	2.50	-5.00

The charge balance appears to be quite good for the analyses of this material/compound, e.g. +5.28 versus -5.32. If the compound is assumed to contain two aluminum atoms in its empirical formula, the compound may be written as:

25 Dye Adsorption

The dye adsorption of C.I. Direct Red 80 for freshly generated sol A was 2800 mg of dye per gram of Al_2O_3 . However, values of nearly 5000 mg per gram of alumina are observed for an "aged" sol retain sample. If it is assumed that an adsorption site exists for every acetate molecule, the number of sites are calculated as 0.0033 moles per gram of alumina, Al_2O_3 . Based on a molecular weight of 1417 gram/mole for Direct Red 80 and one dye molecule per site is adsorbed, the theoretical amount of dye which can be adsorbed is calculated to be 4700 mg per gram alumina. The empirical formula is thus consistent with the adsorption

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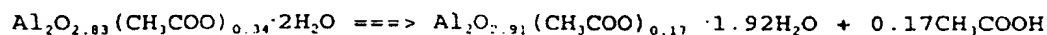
of dye.

Similarly, for sol B the calculated adsorption (assuming one adsorption site per acetate ion) is 0.0062 moles of adsorbent per gram of alumina, Al_2O_3 . For the C.I. Direct Red 80, the anticipated adsorption would be approximately 8800 mg per gram of alumina. Although this is not found in freshly generated sols, "aged" sols of this material have shown adsorptions of 8000 mg per gram of alumina.

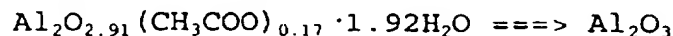
Thermal Analysis

The thermal residual weight of sol A on heating to 650°C is calculated to be 65.66% for the compound resulting in alumina, Al_2O_3 . The measured residual weight was found (Figure 1) to be 69.50% without initial drying. It is suspected that some of the loosely bound acetate is lost as acetic acid at ambient conditions prior to the thermal analysis. For example, if it is assumed that only about half the moles of acetate are truly bonded to the alumina and the remainder is merely absorbed into the solids as acetic acid, the theoretical residual weight for heating $\text{Al}_2\text{O}_{2.91}(\text{CH}_3\text{COO})_{0.17} \cdot 1.92\text{H}_2\text{O}$ is 70.27%.

1) Loss of loosely bound acetic acid and water:



2) Sample heated to 650°C :



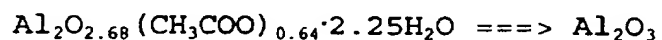
This explanation is consistent with the adsorption of the direct Red 80 dye. For example, the amount of dye adsorbed would be predicted to be about 2400 mg per gram alumina.

Additional samples were prepared by thermal treatment for characterization by infrared spectroscopy. To determine the nature of the chemical components being

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lost at 80°C, the sample of the dried sol was heated at 80°C for 17 hours. The residual weight for this sample was measured as 93.72% (Fig. 2). Similarly, when a sample was heated at 350°C for two hours a residual weight of 77.60% was determined (Fig. 3).

The air dried sample of sol B was examined by thermogravimetric methods. The maximum temperature that the sample was exposed to was 650°C. At that temperature only alumina would be anticipated to remain, as shown below:



The calculated residual weight based on this equation is 58.24%. As can be seen in Figs. 4 and 5, for the two temperature ramping speeds of 20 and 2 degrees per minute, the residual weights were found to be 61.59% and 61.99%, respectively.

Infrared Analyses

The infrared spectra of samples of air dried AMS material were obtained using potassium bromide mulls. Samples were dried 1) at room temperature, 2) at 80°C for 17 hours (see Figure 6) and 3) at 350°C for 2 hours. The ionized acetate salt is clearly shown at approximately 1600 cm⁻¹, giving further evidence that the AMS material is indeed an acetate salt or compound. The spectra of all samples are given in Fig. 7: A) treated at 350°C for 2 hours, B) treated at 80°C for 17 hours and C) the air dried at room temperature. As can be seen in all the spectra, the salt structure is present.

FREQUENCIES (cm ⁻¹)	ASSIGNMENTS	MODE	REFERENCES
3370	-OH, -COOH	stretching	1
3090	-OH (Boehmite)	stretching	1, 2
1580	Ionized carboxyl (salt) C-O Stretching in -C-O-Al	anti- symmetrical stretching	1 3
1474	CH ₃ - (C=O)	stretching	1
1425	Ionized carboxyl (salt)	stretching	1
1070	-OH (boehmite)	bending	1, 2, 4
750	-OH (boehmite)	bending	2
640	Al-O	stretching	2, 4
480	Al-O	stretching	2, 4

- 1) *Handbook of Chemistry and Physics*; Lide, D.R.; Ed.-in-Chief; 73rd ed.; CRC Press, 1993; 9-152.
- 2) *The Infrared Spectra of Minerals*; Farmer, V.C., Ed.; Mineralogical Society, 1974.
- 3) Maksimov, V.N.; Grigor'ev, A.I. *J. Inorg. Chem. USSR (Engl. Transl.)* 1964, 9(4), 559-560.
- 4) *Infrared Spectra of Inorganic Compounds*; Nyquist, R.A.; Kagel, R.O., Ed; Academic Press, 1971.

As is seen from the TGA (Fig. 1), considerable weight loss (16.16%) occurs above 350°C. The weight loss measured above 350°C is the salt given by the following empirical formula, $\text{Al}_2\text{O}_{2.91}(\text{CH}_3\text{COO})_{0.17} \cdot 0.085\text{H}_2\text{O}$, the theoretical weight loss is calculated as 13.24%, which is in good agreement with that measured. Thus, only water is lost at these temperatures and the alumina acetate salts remain relatively intact.

X-Ray Diffraction

The X-ray diffraction of sol A air dried at 25°C showed broad lines consistent with boehmite alumina (Fig. 8). The line broadening is due to the small particles of alumina present in the sample. The major difference observed is found in the first peak at 2-theta of about 14 degrees, e.g. at the d-spacing of

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6.635 angstroms versus 6.110 for the literature value of boehmite. This, of course, would be expected if the acetic acid were clearly bonded to the alumina fiber, e.g. a salt complex.

5 To further explore this peak at $d=6.635$ Å, a second diffractogram was run to verify the d -spacings. As shown in Fig. 9, the identical diffraction was obtained. However, when the sample was dried at 80°C , the d -spacing at 6.6 angstroms moved to 6.375 Å (Fig. 10),
 10 toward that for boehmite. This suggests this salt complex does undergo a thermal reaction at 80°C , consistent with other experimental findings. All these diffraction results are summarized below:

15	140°C/2 Hours Dried 25°C	53°C/0 Hours		Boehmite, AlOOH: literature values
		80°C	25°C	
	6.635/6.597	6.375	6.835	6.110
	3.198/3.190	3.155	3.172	3.164
20	2.355/2.359	2.350	2.332	2.346
				1.980
	1.864/1.867	1.856	1.861	1.860
				1.850
				1.770
25				1.662
				1.527
				1.453
	1.438/1.440	1.437	1.434	1.434
30				1.383

For the dried sample of sol B, several other small peaks are observed in the diffractogram. (See Fig. 11). The most important shift from boehmite alumina occurs at
 35 about 6.8 angstroms and appears to be unique for this alumina acetate salt/complex.

SUMMARY

Elemental analyses, thermal studies, infrared spectroscopy, and X-ray diffraction support the fact that the sol solids are comprised of a unique boehmite alumina acetate salt, having a high degree of cationic charge, or acetate to alumina ratio. The empirical formulae for sols A and B air dried at ambient temperatures consistent with dye adsorption studies, thermogravimetric analyses and infrared spectroscopy are best fit by $\text{Al}_2\text{O}_{2.83}(\text{CH}_3\text{COO})_{0.34}\cdot 2\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_{2.68}(\text{CH}_3\text{COO})_{0.64}\cdot 2.25\text{H}_2\text{O}$.

EXAMPLE 1

A slurry was made with water and basic aluminum acetate (BAA). The amount of BAA used in the slurry varied from about 1% to about 5% (w/w) on the basis of Al_2O_3 . Once the proper amount of water was added, to make a total of 1500 grams, the slurry was stirred via a magnetic stirrer for 10 minutes. This slurry was placed in a Parr Reactor Model 4522M two litre pressure reactor quickly to prevent any settling. The heating rate was set to high and within 30-45 minutes the reactor was at the desired temperature. A 2 to 5 gram sample was taken at this time and additional samples were taken every 30 minutes thereafter.

After the reaction had run for 2 hours at the designated temperature, the reactor was removed from the heat source and cooled to about 70-80°C by using a cooling pump. The reactor was opened, and the birefringent alumina sol was removed and samples taken for physical characterization. The pH, viscosity, and percent acetic acid were measured for each sample. An aliquot of the product sol was characterized for the fiber dimensions via transmission electron microscopy (TEM).

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Table 1 contains the reaction parameters for the experiment generated by a three factor study.

TABLE 1: REACTION PARAMETERS			
Run Number	Temp. °C	Conc. (w/w) % Al ₂ O ₃	Stirring Rate RPM
1	160	3	300
2	140	1	200
3	140	5	100
4	180	1	300
5	180	3	200
6	140	3	100
7	160	3	200
8	180	3	100
9	180	3	300
10	180	5	300
11	140	5	300
12	180	1	100
13	180	1	200
14	160	5	300
15	160	5	200
16	160	1	200
17	160	3	100
18	160	1	300
19	140	1	300
20	140	1	100
21	160	1	100
22	140	3	300
23	180	5	200
24	140	5	200
25	180	5	100
26	140	3	200
27	160	5	100

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From the TEM micrographs, it was determined that three novel shapes of fibers were manufactured (see Table 2). The first were short, wide individual fibers which were made during the low temperature runs. The second were long, curved, hair-like fibers which were obtained at 160°C, and the third were bundles which appear to be large agglomerations of individual fibers.

TABLE 2: INDIVIDUAL FIBER DIMENSION RANGES AND AVERAGES

Run Number	Average Length (nm)	Longest Fiber (nm)	Shortest Fiber (nm)
1	166	662	38
2	98	175	50
3	347	850	50
4	100	200	38
5	178	538	50
6	136	325	50
7	223	938	50
8	140	438	50
9	134	450	50
10	190	762	38
11	611	2275	88
12	192	975	50
13	100	200	38
14	313	1425	62
15	371	912	62
16	86	188	25
17	176	462	50
18	101	200	50
19	112	325	38
20	122	575	50
21	188	1562	50
22	185	862	50

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TABLE 2: INDIVIDUAL FIBER DIMENSION RANGES AND AVERAGES			
Run Number	Average Length (nm)	Longest Fiber (nm)	Shortest Fiber (nm)
23	305	1300	50
24	470	838	125
25	297	788	62.
26	193	1860	62
27	255	750	88

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Table 3 summarizes dimensional data for the bundles. Bundles are agglomerated fibers that have specific properties. Sols containing bundles have a high sedimentation rate. With this separation ability, bundles can be used in applications where a high settling rate can be used to sediment environmentally unfavorable substances.

The products of reactions at 180°C contain a higher percentage of bundles than those at the lower reaction temperatures. Bundles have varied sizes, with widths up to 3.8 microns and lengths to 18.2 microns.

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TABLE 3: BUNDLE DIMENSIONAL AVERAGE DATA					
Run Number	Longest Bundle (micron)	Shortest Bundle (micron)	Widest Bundle (micron)	Narrowest Bundle (micron)	Geometric Median (sq. microns)
1	15.2	1.38	1.38	0.125	1.50
2	5.12	1.38	1.00	0.125	0.714
3	5.25	0.62	0.62	0.125	0.386
4	3.00	0.5	0.75	0.125	0.227
5	11.2	1.12	3.12	0.125	0.963
6	6.12	1.38	2.5	0.125	1.07
7	7.50	0.62	1.12	0.125	0.462
8	8.75	0.88	1.12	0.125	0.940

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TABLE 3: BUNDLE DIMENSIONAL AVERAGE DATA					
Run Number	Longest Bundle (micron)	Shortest Bundle (micron)	Widest Bundle (micron)	Narrowest Bundle (micron)	Geometric Median (sq. microns)
9	13.7	1.12	3.88	0.125	1.05
10	11.88	1.38	1.38	0.125	1.32
11	7.25	1.75	1.5	0.125	0.970
12	1.12	0.62	0.5	0.125	0.210
13	7.00	1.25	1.00	0.125	2.29
14	13.88	1.00	2.25	0.125	1.08
15	16.9	1.75	2.38	0.125	1.66
16	4.12	2.12	0.62	0.250	1.02
17	5.62	1.12	1.50	0.125	0.983
18	11.0	0.88	1.50	0.125	1.07
19	4.62	0.75	0.88	0.125	0.489
20	6.25	2.12	2.12	0.125	1.43
21	6.00	0.75	1.12	0.125	0.849
22	5.62	1.88	1.25	0.250	1.73
23	12.5	1.12	1.25	0.250	1.28
24	9.88	1.25	0.62	0.125	1.01
25	11.9	1.88	0.62	0.125	1.74
26	3.50	2.00	0.62	0.125	0.827
27	18.2	1.38	1.00	0.120	1.04

Table 4 contains physical characterization data of the final product samples obtained. These data, accompanied by the pressure, temperature, and stirring rate recorded by the computer during the reaction, are crucial to the comparison of each run. As shown, both the percent acetic acid, pH and viscosity are dependent on the percent solids concentration of Al_2O_3 . In the 1% Al_2O_3 sols, the percent acetic acid is approximately 2 percent, 3% sols contained about 6.5 percent and the 5% sols had 11 percent acetic acid in the final product.

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The percent acetic acid was determined by titration versus sodium hydroxide. The pH of each sol also varied with concentration. The viscosity varied with concentration and temperature. The 1% sols had a viscosity below the detection limit of the viscometer, and the 5% sols have viscosities up to 16,100 centipoise (cps).

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TABLE 4: SUMMARIZED PHYSICAL DATA OF FINAL PRODUCTS			
Run Number	pH	Acetic Acid, %	Viscosity (cps)
1	3.08	6.65	664
2	3.41	2.21	<15
3	3.22	10.34	12,400
4	3.42	2.27	<15
5	3.10	6.64	<15
6	3.31	6.63	13,200
7	3.20	6.57	55
8	3.10	6.51	<15
9	3.13	6.68	<15
10	2.94	11.28	83
11	3.22	10.99	10,513
12	3.17	2.40	<15
13	3.24	2.21	<15
14	3.10	11.12	16,100
15	3.14	11.00	8,740
16	3.38	2.25	<15
17	3.20	6.40	<15
18	3.41	2.24	<15
19	3.52	2.21	<15
20	3.54	2.21	<15
21	3.31	2.22	<15
22	3.35	6.54	5,810

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TABLE 4:
SUMMARIZED PHYSICAL DATA OF FINAL PRODUCTS

Run Number	pH	Acetic Acid, %	Viscosity (cps)
23	3.00	11.64	526
24	3.25	10.98	3,650
25	3.03	11.10	83
26	3.35	6.60	4,620
27	3.13	11.88	15,600

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The analysis of these data obtained from the experiments showed the following correlations: 1) fiber length can be increased by increasing reaction temperature; 2) fiber width is greater at the lower concentrations; 3) bundle length is larger for higher concentrations; 4) viscosity of the sol is increased with concentration and decreased with increased temperature.

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EXAMPLE 2

A sol was diluted with deionized water to 0.75% w/w concentration alumina and thoroughly mixed. A fabric was weighed before and after treatment to obtain the percent weight pick up. The target pick up was 80 percent of the original pre-treatment weight. The fabric was dried in an oven at 50°C and then dyed in a solution containing 1 gram of dye per liter of solution at ambient temperature. After dyeing, the fabric was placed into the oven to dry and compared visibly to the commercial control (90°C, 10 wt.% NaCl) for intensity and even coloration.

After dyeing fabric with the sols generated in Example 1, certain types of sols gave noticeably superior dye adsorption than others. The sols, prepared at 140°C/2 hours and containing 3% Al₂O₃ and comprising short, thin fibers produced the most promising dye

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adsorption. These fabric samples were analyzed by reflectance spectroscopy commonly used in the textile industry to obtain a K/S value which is an indicator of a substrate's depth of shade (where K is an absorption coefficient and S is a scattering coefficient, see AATCC Evaluation Procedure 6, 1996, AATCC Technical Manual 1996). The K/S values obtained from the fabric that was treated with the short, thin fibers (runs 6 and 22) and dyed was 6.368. The value for a simulated commercially dyed product (e.g., 10% salt at 90°C) was 5.346, therefore, the addition of the aluminum monohydrate sol improved the intensity of the dye on fabric. The reflectance testing procedure is a standard (ASTM) procedure used in the textile industry. By using this test and interpolating the data obtained, it can be determined whether a product or additive enhances the fabric significantly enough to be commercially marketable.

The dye concentration of the supernatant can be determined by using the absorbance obtained and the standard plot. The amount of the dye adsorbed by the sol is the difference between the starting amount of the dye and the amount left in the supernatant. For example, if the diluted supernatant from centrifugation is found to have a concentration of 0.040 mg of dye per gram of the solution, then the ability of this sol to adsorb this dye can be calculated as follows:

amount of excess dye: $0.040 \text{ mg/g} \times 60 \times 200 \text{ g} = 480 \text{ mg}$
amount of dye adsorbed: $600 \text{ mg} - 480 \text{ mg} = 120 \text{ mg}$
adsorption capacity: $120 \text{ mg} / 0.20 \text{ g} = 600 \text{ mg/g}$

where 0.040 mg/g is the dye concentration of the diluted supernatant obtained from the standard plot, 60 is the dilution factor for the supernatant, 200 g is the total weight of the mixture, 600 mg is the starting amount of the dye, and 0.20 g is the amount of AlOOH solid used.

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The result of this example is that one gram of AlOOH solid is able to adsorb 600 mg of this dye.

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TABLE 5: FABRIC DYEING EXPERIMENTS					
Run Number	Initial Wt., g	Wet Wt. After Sol, g	g of Sol	% of Pick Up	Reflectance Run/Control Ratio
Commercial Control	-----	-----	-----	-----	1.00
1	6.72	12.48	5.76	85.71	1.02
2	6.59	12.24	5.65	85.74	1.09
3	5.66	10.31	4.65	82.16	1.00
4	5.56	10.05	4.49	80.76	0.81
5	6.27	11.89	5.62	89.63	0.80
6	5.13	9.25	4.12	80.31	1.19
7	6.35	11.83	5.48	86.30	0.96
8	6.65	12.52	5.87	88.27	0.90
9	5.81	10.99	5.18	89.16	0.75
10	5.85	10.75	4.90	83.76	0.78
11	5.81	10.98	5.17	88.98	0.99
12	6.20	11.34	5.14	82.90	0.52
13	6.35	11.54	5.19	81.73	0.56
14	6.03	11.04	5.01	83.08	0.86
15	6.42	11.37	4.95	77.10	0.92
16	6.65	11.95	5.30	79.70	0.67
17	6.02	10.61	4.59	76.25	0.55
18	5.56	10.15	4.59	82.55	0.70
19	7.08	12.78	5.70	80.51	0.94
20	6.44	12.56	6.12	95.03	0.98
21	6.83	12.72	5.89	86.24	0.74
22	6.79	12.35	5.56	81.89	1.15
23	6.28	11.31	5.03	80.10	0.67
24	6.37	11.37	5.00	78.49	1.05
25	6.49	12.43	5.94	91.53	0.71

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TABLE 5: FABRIC DYEING EXPERIMENTS

Run Number	Initial Wt., g	Wet Wt. After Sol, g	g of Sol	% of Pick Up	Reflectance Run/Control Ratio
26	7.45	13.49	6.04	81.07	0.95
27	7.30	13.48	6.18	84.66	0.98

5 Adsorption from Spent Dye Baths

The general procedure for a dye adsorption experiment normally includes six steps:

- 1) establishing standard Beer's law plot
- 2) preparing dye solutions and, for reactive dyes only, hydrolysis of the dyes
- 3) mixing sols with dye solutions
- 4) separating the dye-adsorbed particle from water
- 5) determining the amount of excess dye
- 6) calculating the amount of dye adsorbed to obtain adsorption capacities.

Preparation of standard plot.

The maximum absorbencies of six known concentration dye solutions were first obtained using UV-Vis spectroscopy. For the values obtained and the corresponding concentrations (mg of dye per gram of total solution), a plot of absorbencies versus concentrations was generated. The quality of the experimental plot was checked and a best-fit line was produced by computer. This line was used for excess dye determination.

Preparation of mixture of sol and dye solution.

Typically, the total weight of the mixture as well as the amount of each component, including dye, sol, 0.1% Polyacrylamide (PAA), and water, are determined before any experiment. The sequence of addition into the container is: dye, water, sol, and PAA. The dye has

to be completely dissolved, however, before the sol can be added. In the cases of reactive dyes, hydrolysis of the dye is a necessary step before the addition of the sol.

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Determination of excess dye.

About 50 ml of the mixture was centrifuged (or filtered) at the maximum velocity for 2.5 hours. The supernatant was then diluted 20 - 120 times (by weight) for the UV-Vis experiment. The dilution used depends on the absorbencies range of the standard plot, normally between 0.2 - 1.5.

Table 5 summarizes the cloth dyeing experiments and indicates that short thin fibers give superior dye adsorption onto the cloth. Run number 6 shows the highest reflectance value; therefore, the best type of fibers to use are, for this purpose, the thin fibers.

EXAMPLE 3

A screening test was done to evaluate the dye adsorption abilities of the 27 sol products obtained from Example 1. The experiments were designed to mix the same amount of the dye with the 27 sol solutions having the same solid concentration. The reduction of the concentration of the dye caused by adsorption of fibrous acetate is then judged by the changes of the absorbencies obtained from UV-Vis spectrometer. In these tests, 10 ml of sol solution (0.75% Al_2O_3 concentration) was mixed with 0.5 ml of dye (C.I. direct red 80) solution of 1 g/L concentration in a 15 ml centrifuge tube. After 2 hours centrifugation, the supernatant was scanned, using a Perkin Elmer Lambda 2 UV-Vis spectrophotometer. The absorbencies of screening tests are listed in Table 6.

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TABLE 6:
ABSORBANCE VALUES OBTAINED FROM
DYE ABSORPTION TESTS

Run Numbers	Absorbance
(Control)	1.543
1	0.2008
2	0.9432
3	0.151
4	n/a*
5	n/a*
6	0.170
7	n/a*
8	n/a*
9	0.1074
10	0.096
11	0.2439
12	n/a*
13	n/a*
14	n/a*
15	0.0895
16	0.1113
17	0.1848
18	0.1007
19	1.0513
20	0.7695
21	0.0897
22	0.4112
23	0.0686
24	0.1629
25	n/a*
26	0.4376
27	0.1973

*n/a - minor absorption that can not be distinguished from the background

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The data in Table 5 and Table 6 shows that while the smaller fibers might adsorb dye better (good results on cloth dyeing experiments), the resulting particles may be too small to be removed from water easily (poor settling rate). A sol product with a high percentage of large bundle was thus chosen for initial adsorption capacity tests reported in this example, taking advantage of the rapid settlement of these bundles. Sol of this type is produced with 3% Al_2O_3 , relatively high reaction temperature (180°C) and long reaction time (over 5 hours).

Experiments were conducted to identify the adsorption capacity of the alumina acetate sol for various dyes. For a typical experiment, 0.600 and 0.500 g of dye was dissolved into 193.73 and 193.83 g of H_2O , respectively. To each dye solution, 5.67 g of sol was added to make the total mixture weight of 200.00 g which was well mixed by shaking the container. A portion of the mixture was then centrifuged for 2.5 hours. For reactive dyes, 45 minutes of a hydrolysis process at 140°F in the pH range of 10.5 - 11.0 was performed before addition of sol. The sols were prepared to have a high percentage of large bundles using the parameters of run #9 in Example 1 but with a reaction time of five hours.

Before the addition into the dye solution, the alumina acetate monohydrate salt sol is stirred for ten minutes or more to ensure homogeneity. Typically, 5.67 g of this sol, which equals 0.20 g of alumina acetate monohydrate fiber was used. The following calculations were used:

Total amount of Al_2O_3 solid:	$0.03 \times 1500 \text{ g} = 45.00 \text{ g}$
Total amount of $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ solid:	$(120 \text{ g}/102 \text{ g}) \times 45 \text{ g} = 52.94 \text{ g}$
% solid as $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$:	$(52.94 \text{ g}/1500 \text{ g}) \times 100\% = 3.35\%$
or:	$5.67 \text{ g} \times 0.0353 = 0.200 \text{ g}$

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To determine the dye adsorption, the excess (unadsorbed) dye was measured using visible spectroscopy. A standard Beer's law plot (absorbencies vs. dye concentration) was first prepared using dye solutions with known concentration. The supernatant resulting from centrifuging the mixture of sol and dye solution was diluted 20-60 times. The excess dye concentration was calculated from the UV-Vis absorbance, based on a standard plot prepared earlier and the amount of adsorbed dye was determined by comparison with the reduction in dye concentration. The absorption capacity was reached when the amount of dye adsorbed became relatively unaffected by the starting dye concentration.

Capacity tests for 5 dyes and results are summarized in Table 7.

TABLE 7: AMOUNT OF DYE ABSORBED (mg) WITH AMS CONTAINING A HIGH PERCENTAGE OF BUNDLES (Run 1)					
Dye Type	Direct	Direct	Basic	Acid	Sulfur
C.I. Name	Yellow 106	Red 80	Red 14	Black 194	Black 1
Conc. #1	492	688	0	345	468
Conc. #2	520	672	54	305	528

Conc. #1 and #2 are the starting concentrations of 2.5 and 3 g/L, respectively.

One concern was the ability to reproduce the sol products. A second batch of alumina acetate sol (Run 2) was made using the reaction parameters of Run 1. Table 8 compares the results of the two sol products prepared using the same reaction parameters.

TABLE 8: AMOUNT OF DYE ABSORBED (mg) WITH DIFFERENT ALUMINA SOLS					
Dye Type	Direct	Direct	Basic	Acid	Sulfur
C.I. Name	Yellow 106	Red 80	Red 14	Black 194	Black 1
Run 1	520	672	54	305	528
Run 2	484	564	84	319	588

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In some cases, NaCl or Na₂SO₄ was used to simulate the production environment. The results are presented in Table 9.

TABLE 9: THE EFFECT OF SALTS ON THE ABSORPTION CAPACITY

Direct Dyes (3g/L)	NaCl 1%	NaCl 0.5%	Na ₂ SO ₄ 1%	Na ₂ SO ₄ 0.5%
C.I. Red 80	636	565	414	414
C.I. Yellow 106	604	520	568	586

EXAMPLE 4

This experiment tested adsorption at a pH of 3, 4, and 5 in order to determine which pH yielded the most adsorption of dye.

Dye solutions were prepared at concentrations of 100 mg/L and the pH adjusted with concentrated HCl or with sodium carbonate (Na₂CO₃), the amount and type of adjustment was determined by earlier experimentation. Alumina acetate sol fiber diluted 60 times and 0.1% PAA were added and the samples centrifuged. Capacity was obtained as described in Example 2.

The sols used in Examples 5, 6, 7, 8 and 9 were prepared using the same reaction parameters as run #6 of Example 1. Frequently, a dilution of this sol was made to enhance the dispersion of the alumina acetate fibers into the dye solution.

TABLE 10

C.I. NAME	RUN NUMBER	ADSORPTION (mg/g)	pH
Direct Red 80	1	2080	3.01
Direct Red 80	2	2020	4.02
Direct Red 80	3	1170	5.80
Direct Yellow 106	4	1890	3.33
Direct Yellow 106	5	1670	4.41

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TABLE 10			
C.I. NAME	RUN NUMBER	ADSORPTION (mg/g)	pH
Direct Yellow 106	6	464	7.00
Acid Yellow 151	7	126	2.97
Acid Yellow 151	8	352	4.08
Acid Yellow 151	9	0	4.82
Acid Black 194	10	1550	2.86
Acid Black 194	11	1150	4.08
Acid Black 194	12	720	5.18
Reactive Black 5	13	363	3.59
Reactive Black 5	14	245	5.00
Reactive Black 5	15	79	6.60
Reactive Red 120	16	1320	2.70
Reactive Red 120	17	892	3.44
Reactive Red 120	18	483	5.01

The data reveals that as the pH of the dye solution approaches 3, the ability of the alumina acetate salt fibers to adsorb dye increases significantly.

EXAMPLE 5

The ability of alumina acetate monohydrate sol fibers to adsorb dye in different concentrations of sodium chloride (NaCl) was assessed. Previous experimentation revealed that adsorption occurs

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favorably at a more acidic pH, therefore the dye solutions were adjusted with concentrated hydrochloric acid (HCl). Some of the dyes precipitate salt at higher concentrations of NaCl, therefore, these dyes were tested at lower concentrations.

Dye solutions were prepared for each of the six dyes tested, the final concentration of the dye being 100 mg/L. The pH of each was adjusted with HCl. Alumina acetate monohydrate sol fibers which had been diluted 60 times and 0.1% polyacrylamide (PAA) were added, the solution centrifuged and analyzed via visible spectroscopy to determine adsorption. (See Example 2).

TABLE 11

RUN NUMBER	C.I. NAME	ADSORPTION (mg/g)	%NaCl	pH
1	Direct Red 80	2080	0	3.01
2	Direct Red 80	2230	2	2.98
3	Direct Red 80	2670	5	2.76
4	Direct Red 80	2890	10	2.63
5	Direct Yellow 106	1890	0	3.33
6	Direct Yellow 106	2180	1	3.06
7	Direct Yellow 106	2280	2	3.07
8	Acid Yellow 151	126	0	2.97
9	Acid Yellow 151	287	1	3.05
10	Acid Yellow 151	326	2	2.94
11	Acid Black 194	1550	0	2.86
12	Acid Black 194	2250	2	2.87
13	Acid Black 194	2310	4	2.84
14	Reactive Black 5	363	0	3.59
15	Reactive Black 5	227	2	3.19
16	Reactive Black 5	135	5	3.21
17	Reactive Black 5	165	10	2.82
18	Reactive Red 120	1320	0	2.70

TABLE 11

RUN NUMBER	C.I. NAME	ADSORPTION (mg/g)	%NaCl	pH
19	Reactive Red 120	2210	2	3.24
20	Reactive Red 120	2380	5	3.05
21	Reactive Red 120	2080	10	3.07

EXAMPLE 6

The ability of the alumina acetate monohydrate fibers to adsorb dye in different concentrations of sodium sulfate (Na_2SO_4) was assessed. Previous experimentation revealed that adsorption occurs favorably at a more acidic pH, therefore the dye solutions were adjusted with concentrated HCl. Some of the dyes precipitate salt at higher concentrations of Na_2SO_4 , therefore, these dyes were tested at lower concentrations.

Dye solutions were prepared for each of the six dyes tested, the final concentration of the dye being 100 mg/L. The pH of each was adjusted with HCl. Alumina acetate monohydrate fibers which had been diluted 60 times and 0.1% PAA were added, the solution then centrifuged and analyzed via visible spectroscopy for a determination of adsorption (as described in Example 2).

TABLE 12

RUN NUMBER	C.I. NAME	ADSORPTION (mg/g)	% Na_2SO_4	pH
1	Direct Red 80	2080	0	3.01
2	Direct Red 80	1420	2	3.75
3	Direct Red 80	1330	5	3.98
4	Direct Red 80	785	10	4.02
5	Direct Yellow 106	1890	0	3.33

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TABLE 12

RUN NUMBER	C.I. NAME	ADSORPTION (mg/g)	%Na ₂ SO ₄	pH
6	Direct Yellow 106	1120	1	3.80
7	Direct Yellow 106	1140	2	3.63
8	Acid Yellow 151	126	0	2.97
9	Acid Yellow 151	36	1	3.62
10	Acid Yellow 151	56	2	3.63
11	Acid Black 194	1550	0	2.86
12	Acid Black 194	1160	2	3.85
13	Acid Black 194	1180	4	3.87
14	Reactive Black 5	363	0	3.59
15	Reactive Black 5	0	2	4.09
16	Reactive Black 5	2	5	4.32
17	Reactive Black 5	0	10	4.51
18	Reactive Red 120	1320	0	2.70
19	Reactive Red 120	355	2	4.15
20	Reactive Red 120	254	5	4.32
21	Reactive Red 120	0	10	4.49

The pH of each solution was measured after samples were obtained for centrifugation. It was found that the addition of the HCl to these solutions did not lower the pH of the solutions to 3, but rather to 4. Therefore, more favorable results, based on experimentation, might be obtained if the pH were lowered to 3.

EXAMPLE 7

This Example tests the ability of alumina acetate monohydrate sol fibers to adsorb dye at temperatures of typical jet dyeing effluents of commercial dye houses.

Control dye solutions, at concentrations of 3g/L, were prepared as normal at ambient temperature. Test

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dye solutions were prepared at 65°C and 85°C and at concentrations of 3g/L. Dye containers and the water used to dilute the dye were heated, and the alumina acetate monohydrate sol fibers were warmed to about 40°C. The solutions and sol were mixed while hot, poured into tubes, and centrifuged while hot. Capacity of the dye solutions were measured by UV - visible spectroscopy as described in Example 2.

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TABLE 13			
RUN NUMBER	C.I. NAME	TEMPERATURE, °C	ADSORPTION (mg/g)
1	Direct Red 80	Ambient	2714
2	Direct Red 80	65°C	2393
3	Direct Red 80	85°C	1995
4	Direct Yellow 106	Ambient	1828
5	Direct Yellow 106	65°C	1324
6	Direct Yellow 106	85°C	1587
7	Acid Yellow 151	Ambient	1549
8	Acid Yellow 151	65°C	850
9	Acid Yellow 151	85°C	669
10	Acid Black 194	Ambient	1724
11	Acid Black 194	65°C	1660
12	Acid Black 194	85°C	1835
13	Reactive Red 120	Ambient	944
14	Reactive Red 120	65°C	0
15	Reactive Red 120	85°C	1166

10

TABLE 13			
RUN NUMBER	C.I. NAME	TEMPERATURE, °C	ADSORPTION (mg/g)
16	Reactive Black 5	Ambient	778
17	Reactive Black 5	65°C	766
18	Reactive Black 5	85°C	371

5

EXAMPLE 8

The standard acrylic latex white liquid coating material was mixed with increasing percentages of alumina acetate monohydrate salt sol. This sol was chosen because of the gloss and yellowing reduction effects observed from previous testing. This sol was very viscous, but easy to mix in the liquid latex coating using an electric laboratory turbine type stirrer.

The liquid latex was coated on plate glass panels and allowed to dry for 48 hours. The percent gloss was measured, and the same panels were exposed to ultraviolet radiation for 48 hours. The following results were observed:

1. The percent gloss decreased significantly with the addition of sol.
2. Addition of colorless sol from 1-11 percent by weight reduced gloss and increased gloss after 11 percent.
3. From micrographs of the coating surfaces, the texture roughens with the addition of sol which decreases gloss; and the texture of UV exposed surfaces does not appear differently than nonexposed surfaces.

The sol was an excellent additive to latex coatings for adjusting the percent gloss. The mechanism of this phenomenon is as follows:

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1. The very hydrophilic and colorless sol was added to a water borne acrylic latex liquid coating which was easily dispersed due to the amount of water present.
- 5 2. When the liquid coating was applied to a substrate, the water evaporated from the coating and the sol, which became incompatible in the absence of water.
- 10 3. The alumina acetate monohydrate particles formed nondispersed microparticles which roughen the surface slightly without an effect on color and disperse light when the gloss is measured.

15 The addition of pigments of selective fineness of grind (particle size) is the standard method of adjusting gloss. This sol is colorless and non-interactive, and has an excellent application as a convenient coatings additive.

20

EXAMPLE 9

Alumina acetate monohydrate salt fibers produced in accordance with Example 1 (Run Number 6) were compared with commercial polyelectrolytes to determine their utility in wastewater treatment.

25

The bench scale tests comparing the alumina acetate monohydrate salt fibers to a variety of inorganic and organic cationic polyelectrolytes were run using the same basic procedure. The product presently in use was run first to establish its dosage and performance level.

30 After the base line was established a series of tests were run using the fibers to establish the dosage range where it gave similar performance to the product presently in use. Once the dosage range for the fibers was established then a series of direct comparison tests

35 were run. Then a final test was run and specific performance characteristics (settling rate, floc size, effluent color and turbidity, etc.) were determined.

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Iron Ore Tailings Clarification

In preparation of iron ore one starts with crude ore and removes the silica using a magnetic separation process. The ore is first ground to minus 500 mesh in a series of wet ball and rod mills and is then passed over a series of magnets. The iron oxide is concentrated on the magnets and separated from the silica. The rejects from the magnetic separators still contain some iron ore and this is recovered in a high rate classifier. The heavier iron ore settles and the lighter silica does not settle and flows out of the system.

The rejects leave the high rate classifiers and are clarified using Poly DADMAC in large diameter clarifiers. The solids in this tailings stream vary from 3% to 5%. These units produce a recycled water quality of 100 +/- 20 turbidity units. The feed rate of liquid Poly DADMAC (20% active) is 1.0 to 1.5 mg/l depending on how many grinding circuits are in operation. At low operating rates the dosage is closer to 1.0 mg/l. This is because there is more time available for settling. At higher rates more material is needed to maintain good recycle water quality.

Graduate cylinder settling tests were run to determine the settling rates of Poly DADMAC and the alumina acetate monohydrate salt fibers. A 5 gallon sample of tailings was collected and the polymer was added to this sample. After mixing this slurry a one liter sample was taken from the 5 gallon sample and added to a one liter graduated cylinder. Time was recorded as the slurry passed the marks on the 1,000 ml graduate. These batch clarification tests were run in the field next to the clarifier. The turbidity recorded were estimates based on direct comparison with known samples.

The following summarizes the data collected using Poly DADMAC and the fibers. The dosage required for the fibers to produce results similar to Poly DADMAC was in

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the 400 to 500 mg/l range.

5 GALLON BATCH CLARIFICATION TESTS

	SAMPLE#	DOSAGE MG/LITER	SETTLING RATES IN SECONDS PER 1.75 INCHES		CLARITY
			FREE SETTLING	COMPACT SETTLING	
			800 ML to 600 ML	500 ML to 300ML	
5	1. Poly DADMAC	1.5	21	23	GOOD
	2. Poly DADMAC	1.0	24	27	FAIR
10	3. Alumina Acetate Monohydrate Salt Fibers	500.0	20	24	GOOD
15	4. Alumina Acetate Monohydrate Salt Fibers	400.0	28	30	FAIR
20	5. Alumina Acetate Monohydrate Salt Fibers	500.0	22	25	GOOD
	6. Poly DADMAC	1.3	23	27	GOOD
25	7. Poly DADMAC	1.0	25	30	FAIR
	8. Alumina Acetate Monohydrate Salt Fibers	400.0	33	60	FAIR
30	9. Alumina Acetate Monohydrate Salt Fibers	500.0	27	33	FAIR
35	10. Alumina Acetate Monohydrate Salt Fibers	600.0	23	26	GOOD

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Wastewater Treatment

For several years municipalities have used high dosages (30 to 40 mg/l) of polyamines to remove color from textile plant wastewater. The polyamine (50% active) is CPS material.

Conventional jar tests were run to determine the performance of the fibers compared to polyamine and Poly Aluminium Chloride (70% and 83% basic). Initial color results were done by comparing one effluent sample to another. In the final series actual colors were run using a color determination procedure which involved triple filtering each sample, running each sample at three different wave lengths and using a computer to calculate the final color. The untreated colors run 600 to 800 where the secondary effluent colors fun between 375 and 425. The following summarizes the results of the tests.

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WASTEWATER TREATMENT PLANT
ONE LITER BATCH CLARIFICATION TESTS

	SAMPLE#	DOSAGE MG/LITER	SETTLING RATES TO 500 ML MARK	SLUDGE VOLUME AFTER 15 MINUTES	CLARITY VISUAL INSTRUMENT
5	1. Polyamine	20	150 sec.	200 ml	400 NR
	2. Polyamine	30	135 sec.	200 ml	300 NR
10	3. Alumina Acetate Monohydrate Salt Fibers	500	180 sec.	220 ml	350 NR
15	4. Alumina Acetate Monohydrate Salt Fibers	1,000	240 sec.	240 ml	300 NR
	5. PAC 70% Basic 23% Al ₂ O ₃	50	180 sec.	200 ml	450 NR
20	6. Polyamine & PAC 70% Basic	15 20	180 sec.	200 ml	250 NR
25	7. Polyamine & Alumina Acetate Monohydrate Salt Fibers	150	200 sec.	220 ml	300 NR
30	8. Polyamine & Alumina Acetate Monohydrate Salt Fibers	20 100	170 sec.	210 ml	300 NR
	9. Polyamine	20	135 sec.	200 ml	400 395
35	10. Polyamine	30	125 sec.	200 ml	300 389
	11. Polyamine PAC 70% Basic	20 20	190 sec.	210 ml	200 394
40	12. Polyamine & Alumina Acetate Monohydrate Salt Fibers	15 150	180 sec.	220 ml	300 385
45	13. Alumina Acetate Monohydrate Salt Fibers	300	160 sec.	210 ml	400 419
50	14. Alumina Acetate Monohydrate Salt Fibers	600	180 sec.	220 ml	300 399

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The alumina acetate monohydrate salt fibers give comparable results to the polyamine at 600 mg/l. The sludge volume was slightly higher and the solids settle slightly slower than the polyamine. The fibers have a large floc like the polyamine whereas the PAC has a very fine floc. The fibers measurably outperform the PAC type products.

The best results were for a combined treatment of Poly Amine (15 to 20 mg/l) and alumina acetate fibers (100 to 150 mg/l). This treatment was run several times and gave excellent results. This is important where a plant is having a toxicity problem and the polyamine is the cause.

Municipal Drinking Water Treatment

Municipalities clarify river water using either Alum or Poly Aluminium Chloro Sulfate (PACS) and switch back and forth from alum to PACS depending on the water quality. The alum is 17% Al_2O_3 and the PACS is a 50% basic product containing 10.5% Al_2O_3 . When the alkalinity is low and the turbidity is high they use PACS. When the alkalinity is high and there is high color in the water they use alum.

All tests were run in a constant temperature bath. Untreated river water had turbidities of 0.17 units. The following summarizes the results obtained. "Floc Formation" is the time in seconds it takes to see a visual pinpoint floc. "Floc Size" is a relative number with the higher numbers designating finer floc with pinpoint floc being a "12". "Clarity" is a relative measure of the clarity of the water with "1" being distilled water and untreated water being "12".

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ONE LITER BATCH CLARIFICATION TESTS

	SAMPLE#	DOSAGE MG/LITER	FLOC FORMATION	FLOC SIZE	CLARITY	TURBIDITY		PH
						UNFILTERED	FILTERED	
5								
	1. Alum	30	180 sec.	7	3	14.7	5.1	6.7
	2. Alum	40	120 sec.	7	2	16.4	1.7	6.6
10	3. Alum	50	60 sec.	8	1	2.2	0.2	6.5
	4. PACS	30	120 sec.	6	2	14.1	2.0	6.7
	5. PACS	45	80 sec.	5	2	1.6	0.3	6.7
15	6. PACS	60	45 sec.	4	1	0.6	0.1	6.6
	7. Alumina Acetate Monohydrate Salt Fibers	100	150 sec.	7	5	7.5	5.0	7.0
	8. Alumina Acetate Monohydrate Salt Fibers	150	60 sec.	5	4	6.0	4.0	7.0
25	9. Alumina Acetate Monohydrate Salt Fibers	200	150 sec.	7	3	5.0	1.5	6.8
	10. Alumina Acetate Monohydrate Salt Fibers	300	180 sec.	9	2	4.2	1.0	6.7
	11. Alumina Acetate Monohydrate Salt Fibers	600	240 sec.	12	1	1.8	0.5	6.2
35								
	12. Alumina Acetate Monohydrate Salt Fibers	900	240 sec.	12	1	2.4	0.1	5.2
40								

The following summarizes the fiber dosages required for good flocculation (DS ONE) and color and turbidity removal (DS TWO) for each application.

5	APPLICATION	PRESENT PRODUCT AND DOSAGE	ALUMINA ACETATE	
			MONOHYDRATE SALT FIBER	
			<u>DS ONE</u>	<u>DS TWO</u>
	Iron Ore Tailings	Poly DADMAC (20%) 1.0 - 1.5 mg/l	400-50 mg/l	400-500 mg/l
10	Wastewater Treatment	Polyamine (50%) 25-35 mg/l	100-150 mg/l	450-600 mg/l
15	Municipal Drinking Water Treatment	Poly Aluminium Sulfate (10.5% Al_2O_3) 30-45 mg/l	125-175 mg/l	400-600 mg/l

The alumina acetate monohydrate salt fibers worked in all three applications. It performed more like an organic polyelectrolyte (Poly DADMAC and polyamines) than inorganic products (alum, PAC and Poly Aluminium Chloro Sulfate). The fibers have excellent floc forming characteristics, forming a good floc at lower dosages, but requires higher dosages to obtain color and turbidity removal.

CLAIMS

1. A cationic fibrous acetate salt of boehmite alumina obtainable by: stirring a slurry of water and
5 basic aluminum acetate to ensure substantially complete mixing thereof; and reacting the slurry to produce a fibrous cationic acetate salt of boehmite alumina having a zeta potential of greater than about 25 and a weight ratio of aluminum to acetate of less than about
10 4.
2. A salt as claimed in claim 1 having at least about 40% more active/reactive sites than commercial colloidal alumina.
15
3. A salt as claimed in claim 1 or claim 2 wherein said fibres are at least partly in the form of bundles.
4. A salt as claimed in any preceding claim wherein
20 the slurry is reacted at a temperature of from about 100° to about 180°C.
5. A salt as claimed in any preceding claim wherein the slurry is reacted at a temperature of from about
25 140°C to about 160°C.
6. A salt as claimed in any preceding claim wherein the slurry is reacted at a temperature of about 140°C.
- 30 7. A salt as claimed in any of claims 1 to 4 wherein the slurry is reacted at a temperature of about 180°C.
8. A salt as claimed in claim 6 wherein the slurry is reacted for about 2 hours.
35
9. A salt as claimed in claim 7 wherein the slurry is reacted for about 5 hours.

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10. A method for preparing a cationic fibrous acetate salt of boehmite alumina comprising: stirring a slurry of water and basic aluminum acetate to ensure substantially complete mixing thereof; and reacting the slurry to produce a fibrous cationic acetate salt of boehmite alumina having a zeta potential of greater than about 25 and a weight ratio of aluminum to acetate of less than about 4.
11. A process for dyeing fibres with a dye selected from the group consisting of direct, reactive, sulfur and acid dyes comprising: passing undyed fibers through a bath containing dye which is associated with or attached to a cationic fibrous acetate salt of boehmite alumina as claimed in any of claims 1 to 9 whereby the fibers remove the dye from the fibrous acetate salt of boehmite alumina upon contact therewith.
12. A flocculating or precipitating agent comprising a cationic fibrous acetate salt of boehmite alumina as claimed in any of claims 1 to 9 optionally together with one or more components selected from the group which consists of inorganic salts, coagulants, organic flocculants, polymeric flocculants.
13. A process for treating a dye waste stream comprising the steps of: introducing into the stream at least one flocculating or precipitating agent comprising a cationic fibrous acetate salt of boehmite alumina as claimed in any of claims 1 to 9; forming a precipitate or flocculant of the dye and agent; and separating said precipitate or flocculant from the stream.
14. A process as claimed in claim 13 wherein said agent has an ionic charge opposite to that of the dye in the waste stream.

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15. A process as claimed in either of claims 13 or 14 wherein said agent has a positive ionic charge and said dye has a negative ionic charge.
- 5 16. A process as claimed in any of claims 13 to 15 comprising the step of adjusting the pH of the waste stream to between about 2 and about 8.
- 10 17. A process as claimed in any of claims 13 to 16 comprising the step of adjusting the pH of the waste stream to about 3.
- 15 18. A process as claimed in any of claims 13 to 17 comprising the step of separating and regenerating the dye from the flocculant or precipitate.
- 20 19. A process for removing contaminants from a municipal waste treatment stream comprising: adding to the stream a cationic fibrous acetate salt of boehmite alumina as claimed in any of claims 1 to 9; forming a precipitate or flocculant of the contaminants and the salt; and separating the precipitate or flocculant from the waste stream.
- 25 20. A process as claimed in claim 19 comprising the step of adjusting the pH of the waste stream to between about 2 and about 8.
- 30 21. A flocculating agent for use in waste treatment comprising a salt as claimed in any of claims 1 to 9 together with polyamine.

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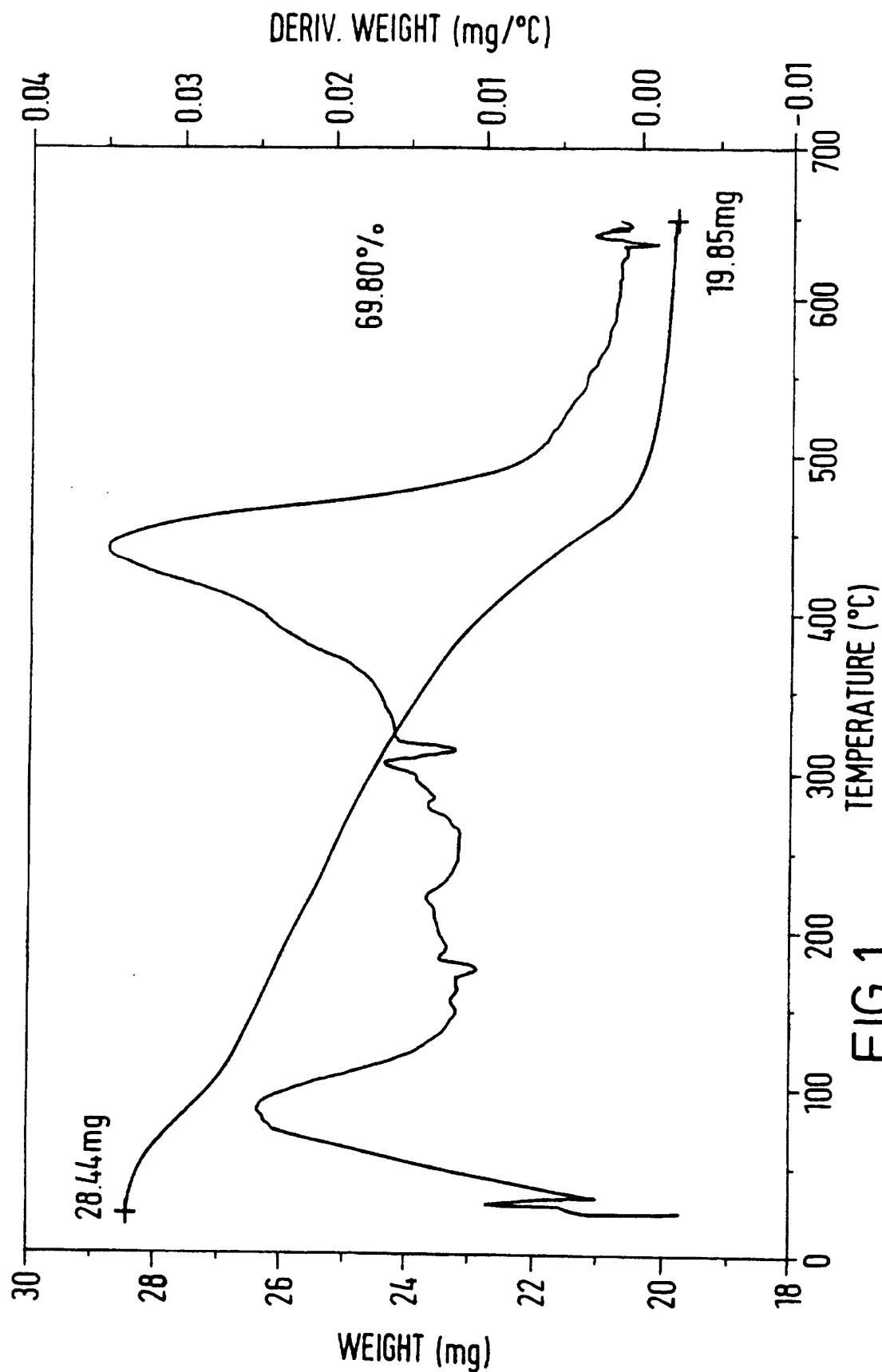
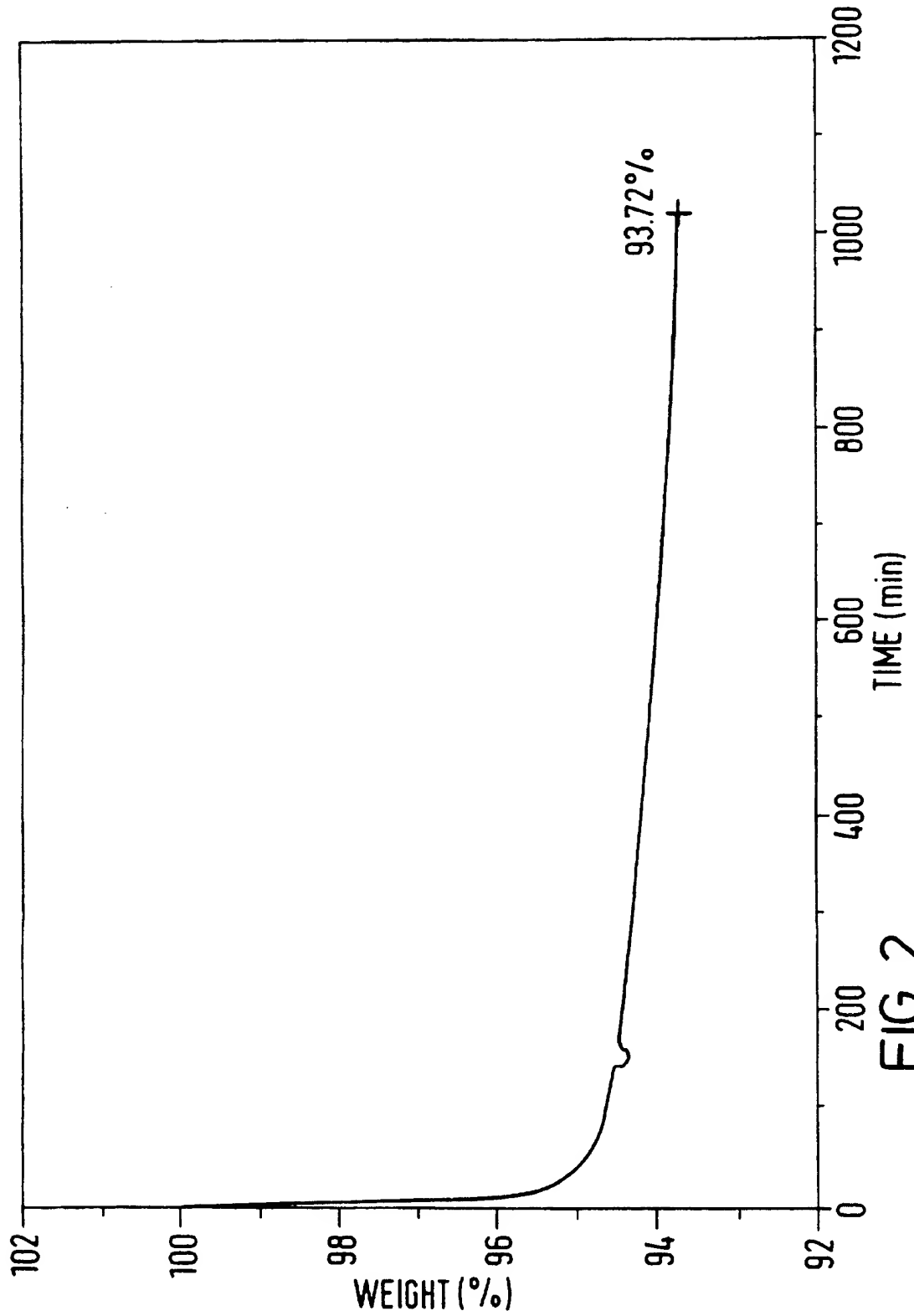


FIG. 1

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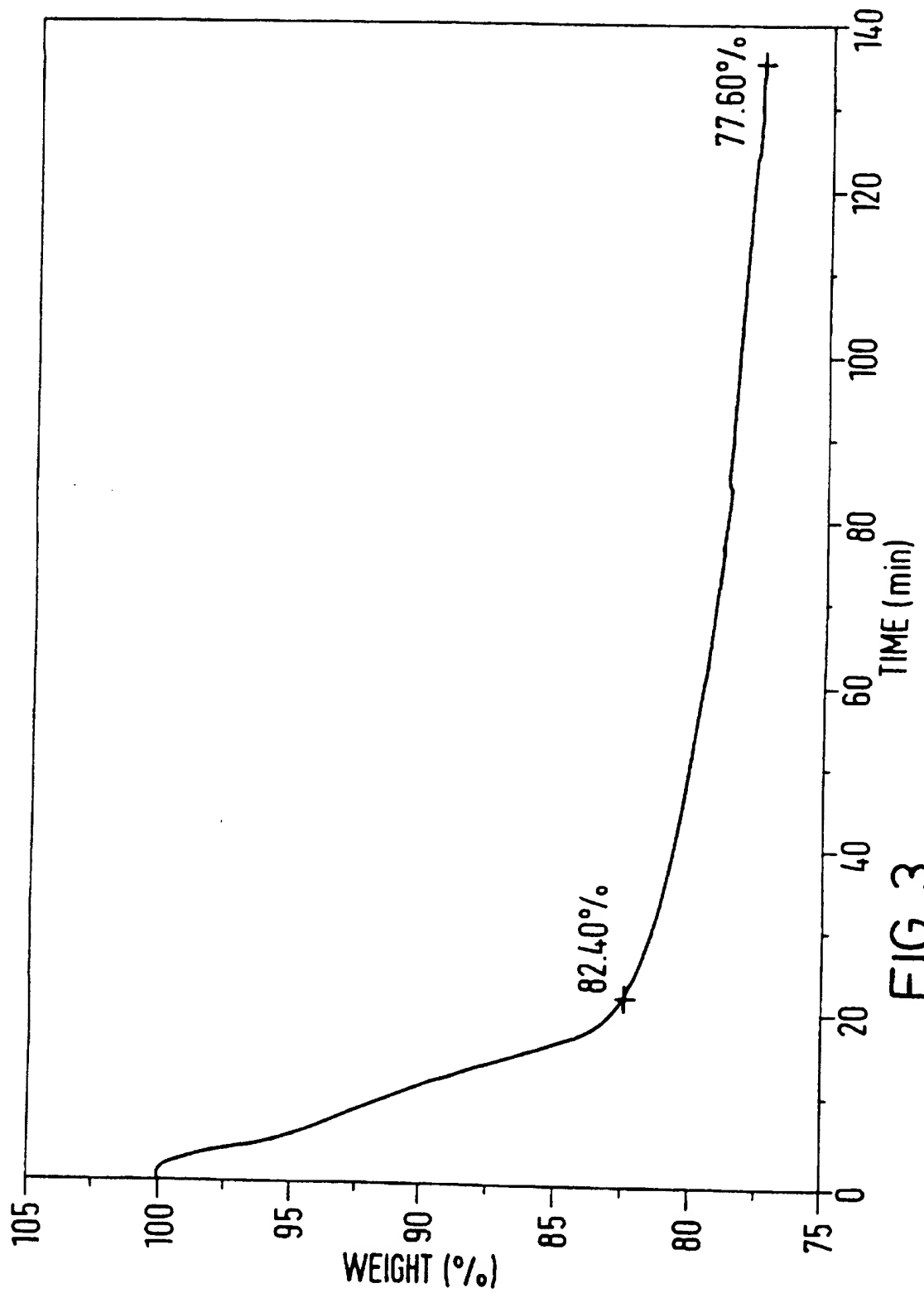


FIG. 3

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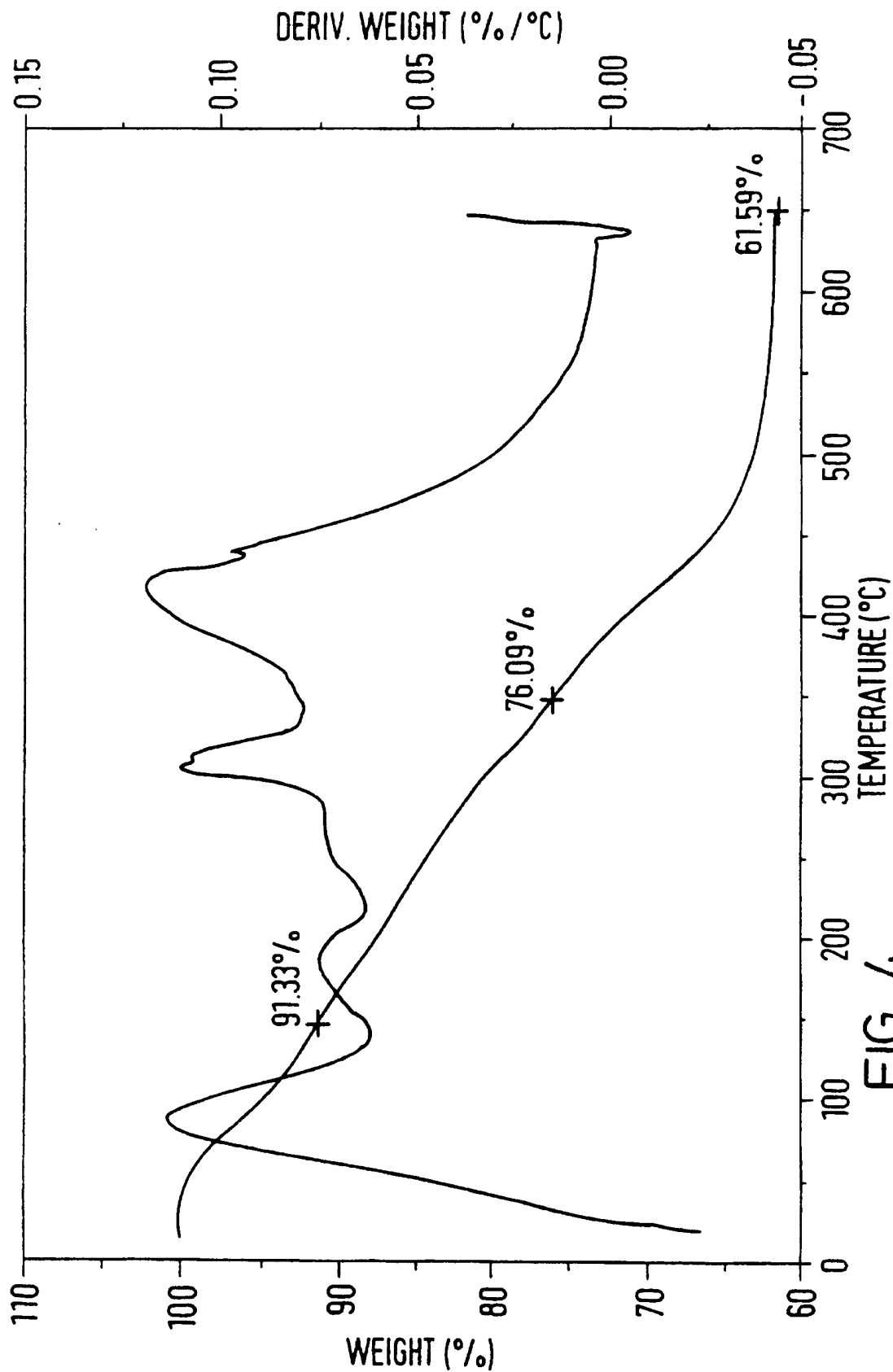


FIG. 4

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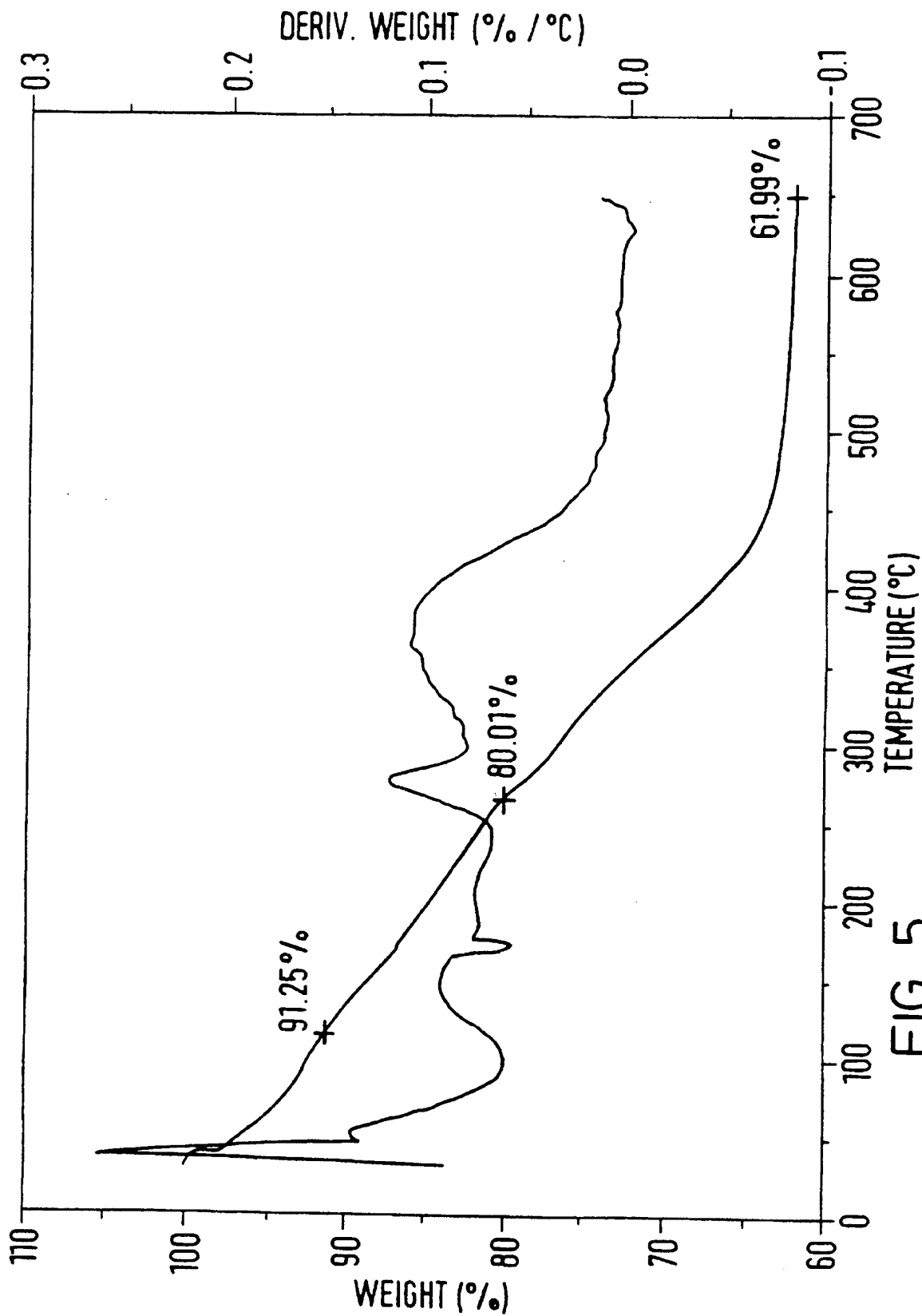


FIG. 5

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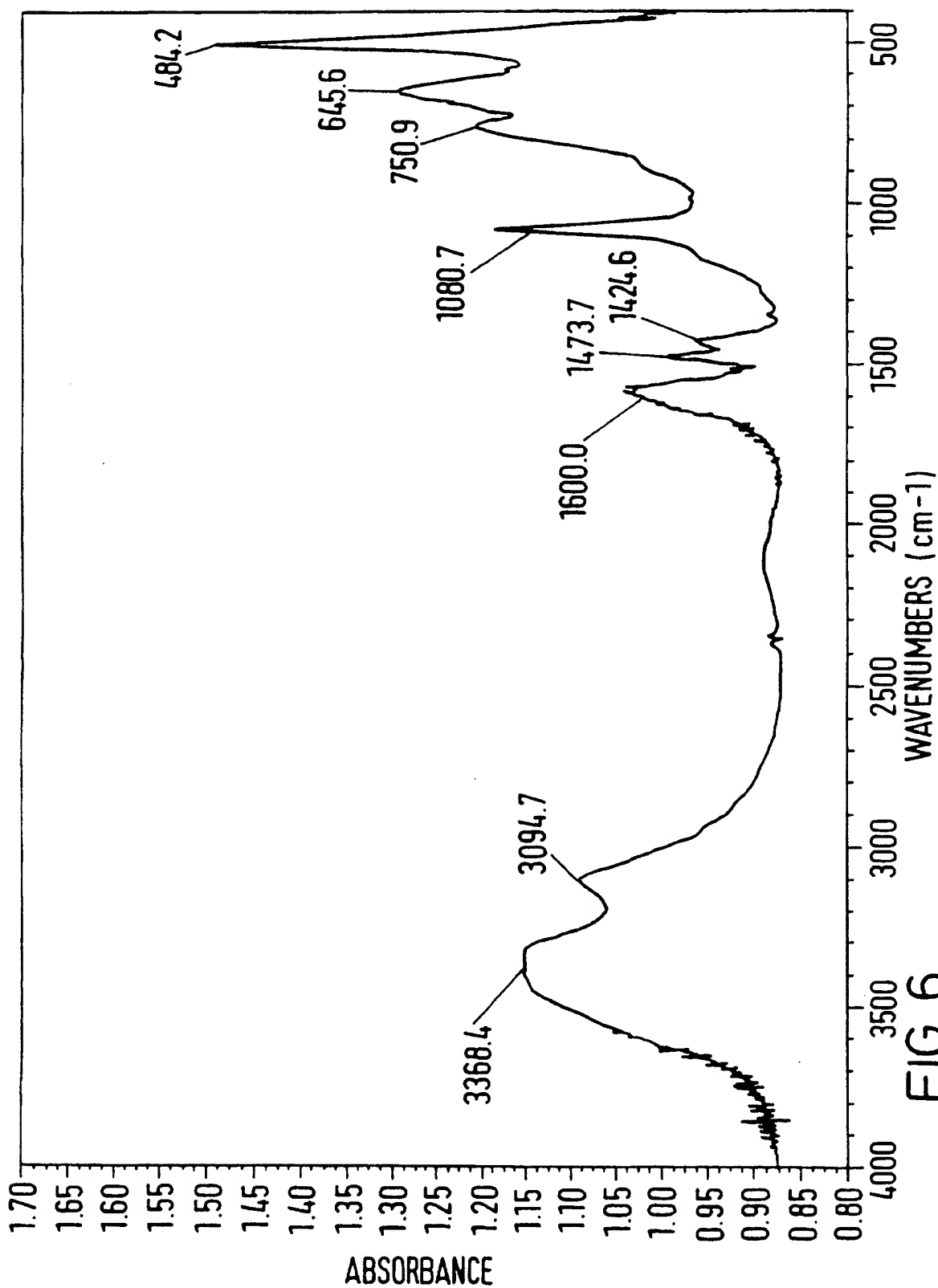
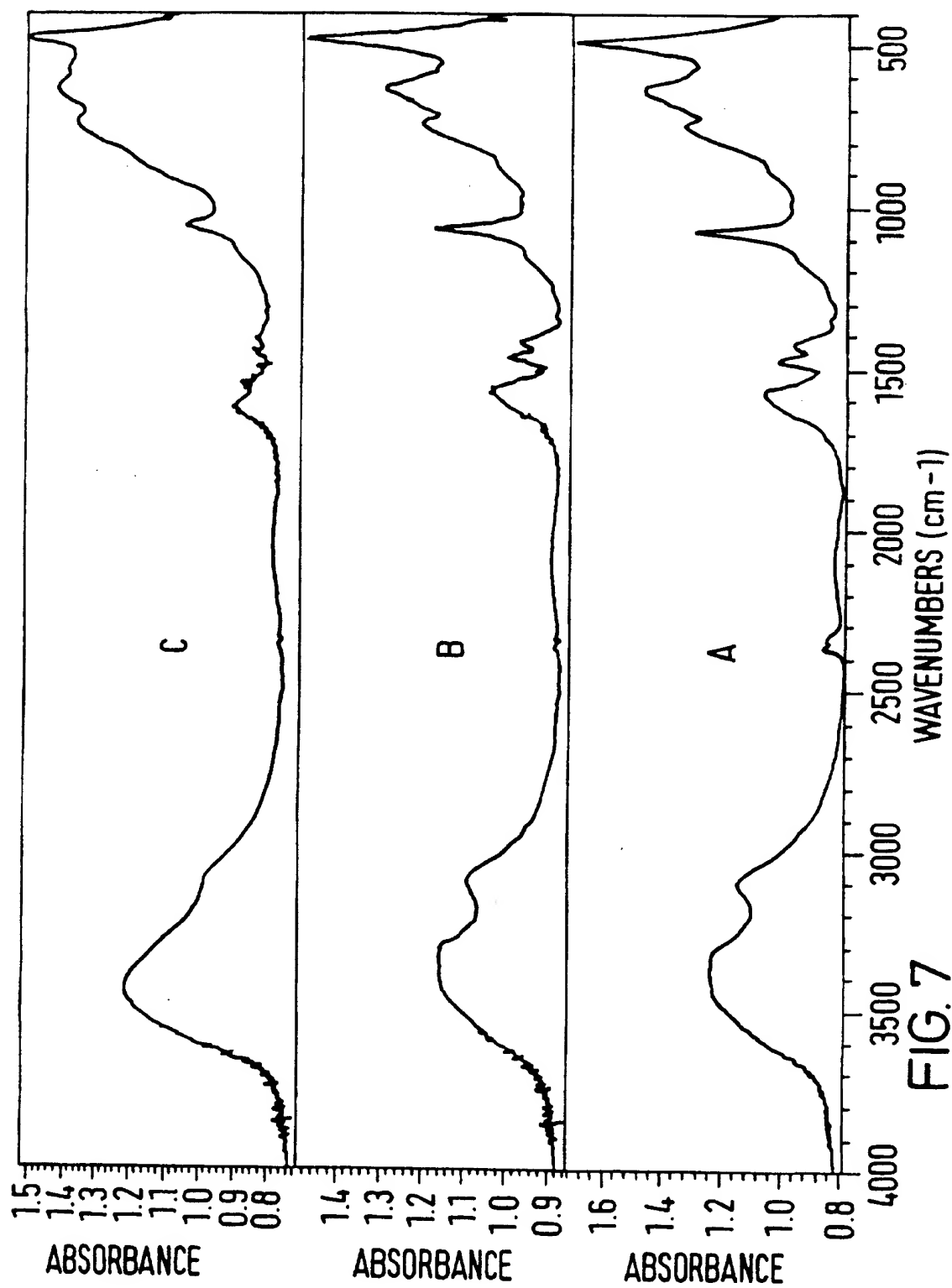


FIG. 6

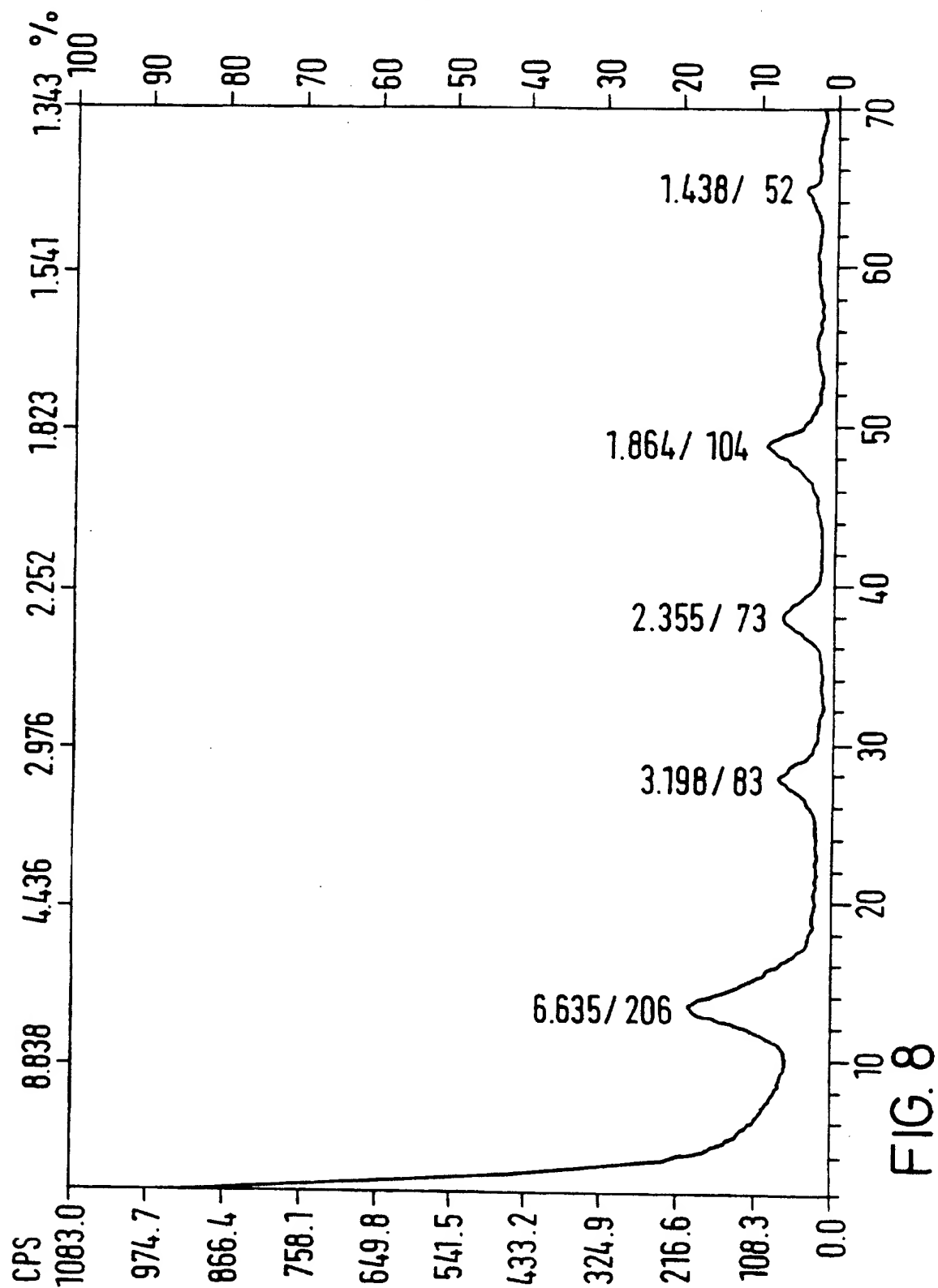
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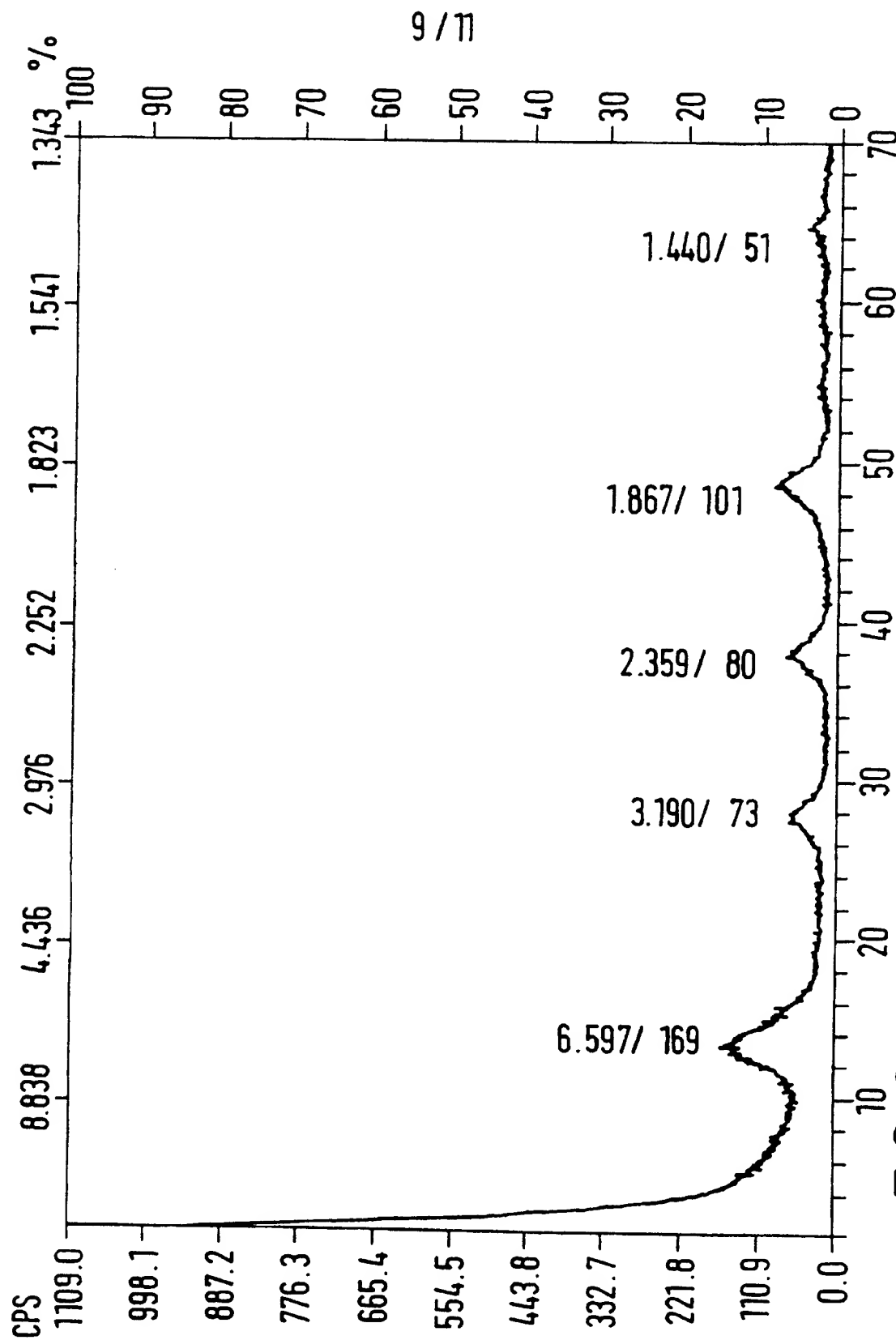


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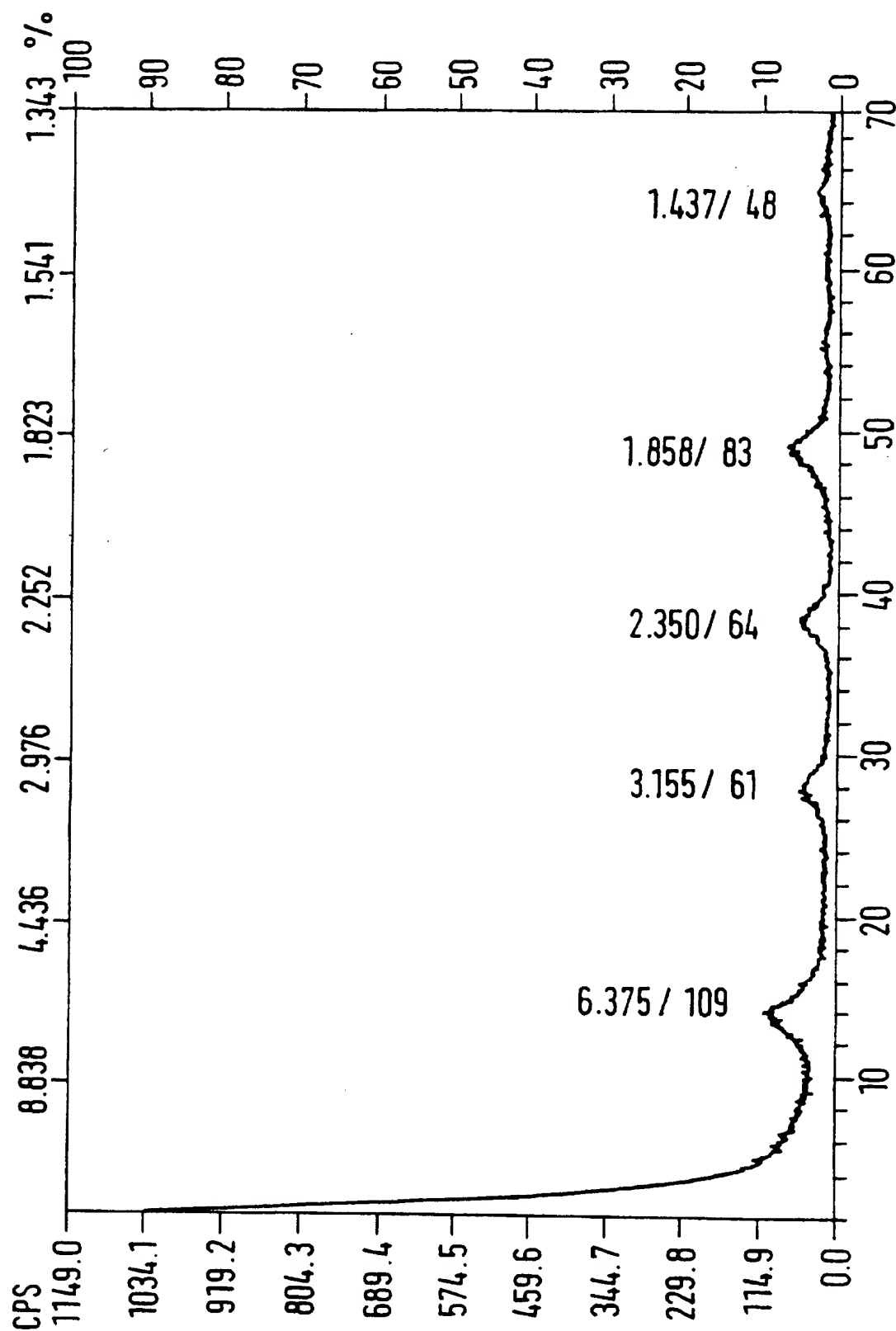


FIG. 10

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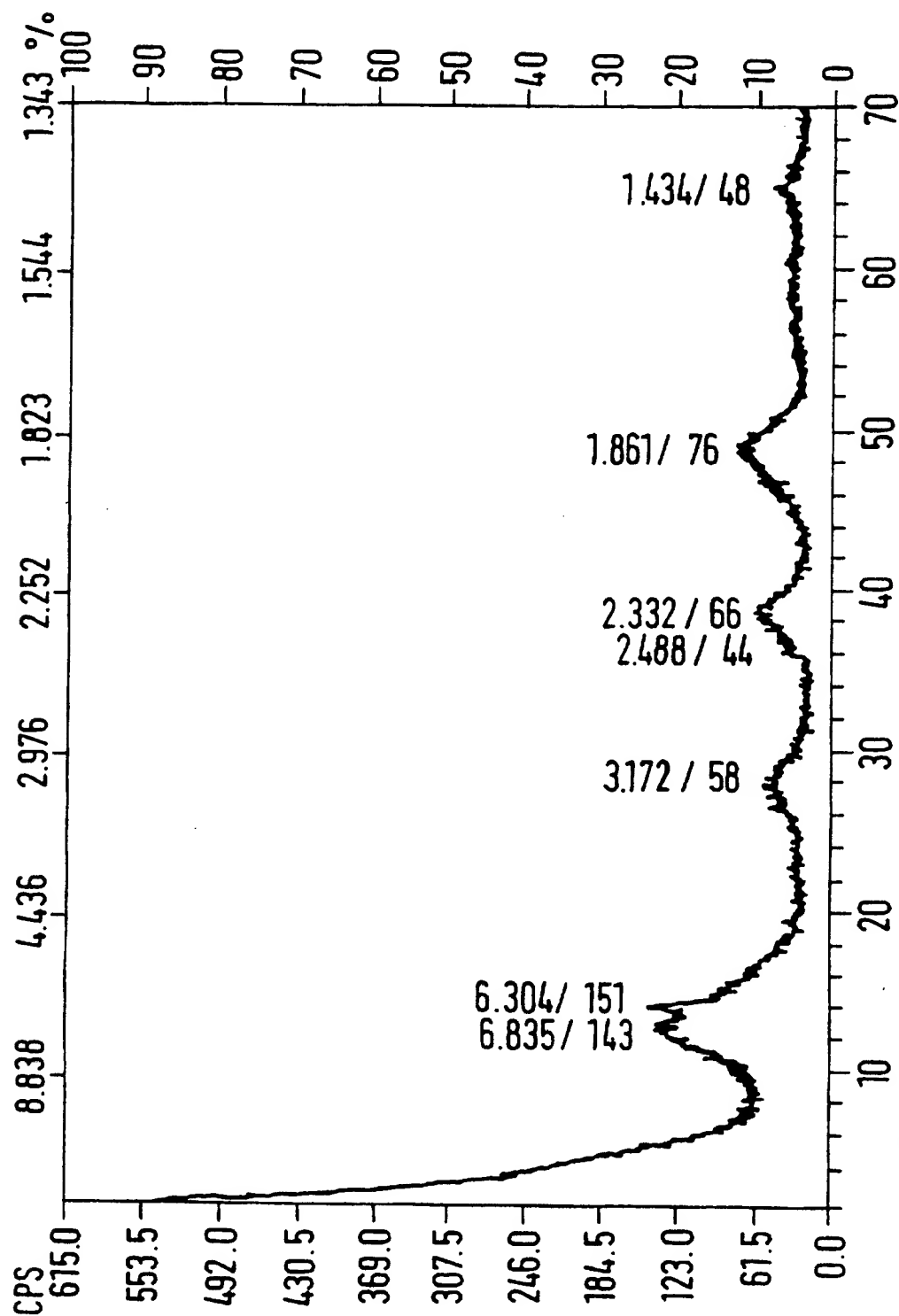


FIG. 11

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/01170

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01F7/02 C01F7/00 C09B69/02 D06P1/673 D06P1/653

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01F C09B D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 790 495 A (PODSCHUS E) 5 February 1974	1-11
Y	see column 3, line 59 - line 73; claims	12-20

X	EP 0 140 448 A (PHILIPS NV) 8 May 1985	1,2,10
Y	see page 2, line 34 - page 3, line 14; claim 3	12-20

X	DE 14 67 260 A (CONTINENTAL OIL COMPANY) 13 March 1969	1-11
Y	see the whole document	12-20

X	EP 0 015 196 A (RHONE POULENC IND) 3 September 1980	1-11
Y	see the whole document	12-20

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

4 September 1997

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/01170

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 986 760 A (UNITED MERCHANTS AND MANUFACTURERS) 24 March 1965	1-11
Y	see page 2, line 81 - line 101; claims	12-20
X	EP 0 505 896 A (NORTON CO) 30 September 1992	1,2,4-10
Y	see page 2, line 52 - line 54; claims; example 5	12-20
X	CHEMICAL ABSTRACTS, vol. 81, no. 6, 12 August 1974 Columbus, Ohio, US; abstract no. 32638, BUMANS, R. ET AL: "Effect on the concentration of acetic acid on hydrothermal synthesis of boehmite from bayerite and hydrargillite" XP002039528	1-9
Y	see abstract & LATV. PSR ZINAT. AKAD. VESTIS, KIM. SER. (1974), (2), 167-70 CODEN: LZAKAM,	12-20
Y	EP 0 342 339 A (CONDEA CHEMIE GMBH) 23 November 1989 see the whole document	12-20

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/01170

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3790495 A	05-02-74	BE 778863 A	02-08-72
		DE 2104897 A	17-08-72
		FR 2124451 A	22-09-72
		GB 1328052 A	30-08-73
		NL 7201250 A	07-08-72

EP 0140448 A	08-05-85	NL 8303685 A	17-05-85
		JP 60121645 A	29-06-85
		US 4576833 A	18-03-86

DE 1467260 A	13-03-69	BE 670286 A	17-01-66
		CH 448982 A	11-04-68
		FR 1409781 A	08-12-65
		GB 1022944 A	
		NL 6407784 A	12-01-65

EP 0015196 A	03-09-80	FR 2449650 A	19-09-80
		BR 8001095 A	29-10-80
		CA 1153187 A	06-09-83
		JP 1240927 C	26-11-84
		JP 55116622 A	08-09-80
		JP 59013446 B	29-03-84
		US 4344928 A	17-08-82

GB 986760 A		US 3240553 A	15-03-66

EP 0505896 A	30-09-92	US 5178849 A	12-01-93
		AU 641082 B	09-09-93
		AU 1100292 A	28-01-93
		CA 2061112 A	23-09-92
		DE 69214335 D	14-11-96
		DE 69214335 T	24-04-97
		JP 5070121 A	23-03-93

EP 0342339 A	23-11-89	DE 3817251 A	23-11-89
		CA 1326434 A	25-01-94
		ES 2053845 T	01-08-94
		JP 2018492 A	22-01-90
		JP 7047729 B	24-05-95
		US 4992199 A	12-02-91